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3. WO 99/29829

Detergent particles having good dissolution rate

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Abstract (Basic): WO 9929829 A1

NOVELTY - Detergent particles having good dissolution rate have pores capable of releasing bubbles from inner portion in process of dissolving particles in water

DETAILED DESCRIPTION - Detergent particles have an average particle size of 150-500 microns, a bulk density of 500 g/l or more and have pores capable of releasing bubbles from an inner portion of the particles in a process of dissolving them in water. The bubbles have a size of one-tenth or more of a particle size of the detergent particles, and the particles have a dissolution rate of 82% or more, under conditions where they are supplied to water at 5 degreesC, stirred for 30s under the following conditions:

(i) 1 g of the particles is supplied to a one-liter beaker having an inner diameter of 105 mm and charged with one-liter of hard water containing 71.2 mg. CaCO₃/l. The mol ratio of Ca/Mg is 7/3; and

(ii) The mixture is stirred with a stirring rod of 35 mm in length and 8 mm in diameter at a rotational speed of 800 rpm, and filtered with a standard sieve having a sieve opening of 74 microns as defined by JIS Z 8801.

The dissolution rate is calculated by the Equation (1) Dissolution rate (%) = $(1 - (T/S)) \times 100$ S = wt. in g. of detergent particles supplied; T = dry wt. in g. of remaining insolubles of the particles on the sieve when a liquid under the above stirring conditions is filtered with the sieve. The drying conditions for the remaining insolubles are heating at 105 degrees C for 1 hour, and then drying in a desiccator containing silica gel at 25 degrees C for 30 min.

INDEPENDENT CLAIMS are also included for:

(1) A method for producing the detergent particles as above comprising:

(a) preparing a slurry containing a water-insoluble inorganic compound, a water-soluble polymer and a water-soluble salt, wherein 60 wt. % or more of the water-soluble components including the polymer and the salt is dissolved in the slurry;

(b) spray-drying the slurry from step (a) to prepare base particles; and

(c) adding a surfactant to the base particles in step (b) to support the surfactant; and

(2) A detergent composition comprising the detergent particles as above in an amount of 50 wt. % or more.

USE - The detergent particles are useful in laundry detergent compositions.

ADVANTAGE - The detergent particles have high-speed dissolution and are capable of dissolving quickly in the water after supplying the particles. The particles also exhibited improved flowability and non-caking properties.

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(54) Title: DETERGENT PARTICLES AND METHOD FOR PRODUCING THE SAME (57) Abstract Detergent particles having an average particle size of from 150 to 500 μ m, wherein the detergent particles have a bulk density of 500 g/liter or more, wherein the detergent particles have pores capable of releasing bubbles from an inner portion of the detergent particles in a process of dissolving the detergent particles in water, the bubbles having a size of one-tenth or more of a particle size of the detergent particles, and wherein the detergent particles have a dissolution rate of 90 % or more under specific conditions.		

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DESCRIPTION

DETERGENT PARTICLES AND METHOD FOR PRODUCING THE SAMETECHNICAL FIELD

5 The present invention relates to detergent particles having high-speed dissolution and a method for producing the same.

BACKGROUND ART

10 Recently, in order to meet the consumers' need "to speedily finish laundry," the commercially available washing machines have the tendency of having large volumes, i.e. large amounts of laundry can be done at one time, and a short washing cycle where washing is completed
15 in a period of about one-half that of the conventionally required washing time is provided. In addition, in order to meet the consumers' need "to carefully wash the clothes," a gentle stirring cycle is arranged, thereby making it possible to reduce the clothes damaging. In
20 addition, in order to meet environmental problems and energy-saving problems and have economic advantages, the trends for saving water, low-temperature washing and shortening of operation time have been considered today, which would become increasingly important in the future.

25 All of these trends have the tendency to decrease the

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amount of work, which is a product of mechanical power and time, of the washing machines. By combinations of such conditions as increasing volume, shortening washing time, lowering mechanical power, saving water, and using cold water, the amount of work can be remarkably reduced. As a result, there arise some crucial problems including deterioration of detergency owing to a drastic decrease in the dissolution rate of the detergent particles, and increasing concern for insolubles of powdery detergents at completion of washing cycle to remain on clothes.

As a prior art in an attempt to solve these problems, Japanese Patent Laid-Open No. 5-247497 discloses a method of producing a detergent composition having a high dissolution property, comprising, upon the preparation of a crutcher slurry including zeolite, adding a citrate and spray-drying the mixture to obtain beads with improved strength, and applying a surfactant on the beads.

In addition, Japanese Unexamined Patent Publication No. 3-504734 discloses a granular adsorbent including 45 to 75% by weight of zeolite, 1 to 6% by weight of a soap, 1 to 12% by weight of a polymer, 0 to 25% by weight of sodium sulfate, 0 to 5% by weight of a nonionic surfactant, and 10 to 24% by weight of water, and supporting a surfactant by its high adsorption ability, wherein the granular adsorbent by which the surfactant is

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supported has a good distributive behavior into the washing machine.

However, in these publications, the above technological problems cannot be solved, and in particular, these publications do not disclose a technology intending to produce detergents which can dissolve at high speeds.

Therefore, as to typical powdery detergents which have been made commercially available, their dissolution rates after 60 seconds and 30 seconds supplying the powder detergent to water at 5°C as defined in the present invention is measured by the method set forth in the present specification. As result, the dissolution rates after 60 seconds for detergents made commercially available in Japan, typical nine compact-type detergents, are in the range from 64 to 87%; the dissolution rates for detergents made commercially available in the U.S., typical four compact-type detergents, are in the range from 75 to 88%; the dissolution rates for detergents made commercially available in Europe, typical three compact-type detergents, are in the range from 57 to 70%; and the dissolution rates for detergents made commercially available in Asia and Oceania, typical two compact-type detergents, are in the range from 64 to 69%. And the dissolution rates after 30 seconds for detergents made

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commercially available in Japan, typical nine compact-type
detergents, are in the range from 55 to 73%; the
dissolution rates for detergents made commercially
available in the U.S., typical four compact-type
5 detergents, are in the range from 65 to 81%; the
dissolution rates for detergents made commercially
available in Europe, typical three compact-type
detergents, are in the range from 40 to 60%; and the
dissolution rates for detergents made commercially
10 available in Asia and Oceania, typical two compact-type
detergents, are in the range from 55 to 60%. The extent
of the dissolution rates obtained above cannot be said to
sufficiently meet the trends for demands in low-mechanical
power mentioned above.

15 Accordingly, an object of the present invention is to
provide detergent particles having high-speed dissolution
capable of dissolving quickly in water after supplying the
detergent particles in water, and a method for producing
the detergent particles.

20

DISCLOSURE OF THE INVENTION

The present invention pertains to the following:

[1] detergent particles having an average particle size
of from 150 to 500 μm , wherein the detergent particles
25 have a bulk density of 500 g/liter or more, wherein the

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detergent particles have pores capable of releasing bubbles from an inner portion of the detergent particles in a process of dissolving the detergent particles in water, the bubbles having a size of one-tenth or more of a particle size of the detergent particles, and wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions (hereinafter simply referred to as "test stirring conditions") that 1 g of the detergent particles is supplied to a one-liter beaker having an inner diameter of 105 mm and charged with one-liter of hard water having 71.2 mg CaCO₃/liter, wherein a molar ratio of Ca/Mg is 7/3, and stirred with a stirring rod of 35 mm in length and 8 mm in diameter at a rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 μm as defined by JIS Z 8801, or wherein the detergent particles have a dissolution rate of 82% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 30 seconds under the test stirring conditions, wherein the dissolution rate is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \quad (1)$$

wherein S is a weight (g) of the detergent particles supplied; and T is a dry weight (g) of remaining

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insolubles of the detergent particles remaining on the sieve when a liquid prepared under the test stirring conditions is filtered with the sieve, wherein drying conditions for the remaining insolubles are keeping at a temperature of 105°C for 1 hour, and then in a desiccator containing a silica gel therein at 25°C for 30 minutes;

[2] detergent particles comprising uni-core detergent particles, each of which comprises a base particle comprising a water-insoluble inorganic compound, a water-soluble polymer and a water-soluble salt, and a surfactant supported by the base particle, wherein the uni-core detergent particles have an average particle size of from 150 to 500 μm , wherein the uni-core detergent particles have a bulk density of 500 g/liter or more, wherein the base particle has a localized structure in which larger portions of the water-soluble polymer and the water-soluble salt are present near the surface of the base particle rather than in the inner portion thereof, and wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the test stirring conditions; and filtered with a standard sieve having a sieve-opening of 74 μm as defined by JIS Z 8801, or wherein the detergent particles have a dissolution rate of 82% or more, under conditions

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where the detergent particles are supplied in water at 5°C; stirred for 30 seconds under the test stirring conditions, wherein the dissolution rate is calculated by Equation (1);

- 5 [3] a method for producing the detergent particles as defined in item [1] or item [2] above, comprising the steps of:

10 Step (a): preparing a slurry containing a water-insoluble inorganic compound, a water-soluble polymer, and a water-soluble salt, wherein 60% by weight or more of water-soluble components including the water-soluble polymer and the water-soluble salt is dissolved in the slurry;

15 Step (b): spray-drying the slurry obtained in Step (a) to prepare base particles containing a water-insoluble inorganic compound, a water-soluble polymer, and a water-soluble salt; and

20 Step (c): adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby; and

[4] a detergent composition comprising the detergent particles as defined in item [1] or item [2] above in an amount of 50% by weight or more.

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BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus, are not limitative of the present invention, and wherein:

Figure 1 is a graph showing comparative results of FT-IR/PAS measurements of Base Particles 1 retaining the original state and in a uniformly ground state;

Figure 2 is a photomicrograph showing a particle structure of Base Particles 1 by SEM (magnification: $\times 400$);

Figure 3 is a photomicrograph showing a particle structure of Base Particles 1 by EDS analysis, i.e. Na distribution (magnification: $\times 400$);

Figure 4 is a photomicrograph showing a particle structure of Base Particles 1 by EDS analysis, i.e. Al distribution (magnification: $\times 400$);

Figure 5 is a photomicrograph showing a particle structure of Base Particles 1 by EDS analysis, i.e. Si distribution (magnification: $\times 400$);

Figure 6 is a photomicrograph showing a particle structure of Base Particles 1 by EDS analysis, i.e. S distribution (magnification: $\times 400$);

Figure 7 is a photomicrograph showing a particle

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structure of the uni-core detergent particles of Example 1
by SEM (magnification: x400);

Figure 8 is a photomicrograph showing a particle
structure of Base Particles 1 by SEM (magnification:

5 x400);

Figure 9 is a photomicrograph showing a particle
structure of Base Particles 2 by SEM (magnification:
x400);

Figure 10 is a photomicrograph showing a particle
structure of Base Particles 3 by SEM (magnification:
x400);

Figure 11 is a photomicrograph showing a particle
structure of Base Particles 4 by SEM (magnification:
x400); and

Figure 12 is a photomicrograph showing a particle
structure of the uni-core detergent particles of Example 2
by SEM (magnification: x400).

BEST MODE FOR CARRYING OUT THE INVENTION

20 1. Mechanism of High-Speed Dissolution

1.1 High-Speed Dissolution by Releasing Bubbles

Conventional compact detergent particles require a
relatively longer period of time for complete dissolution
because they show dissolution behavior in which the

25 detergent particles gradually dissolve from a portion near

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the surface of the detergent particles.

On the other hand, the detergent particles of the present invention are characterized in that in a process in which the detergent particles are dissolved in water, when a small amount of water is firstly entered into the inner portion of the detergent particles, bubbles having a given size are released from the inner portion of the particles at the same time, and subsequently the particles themselves undergo breakdown by entering of a large amount of water into the inner portion of the particles, so that not only the dissolution takes place from a portion near the surface but also the dissolution and breakdown from the inner portion of the particles take place.

The dissolution behavior described above can be confirmed by a digital microscope or optical microscope as a phenomenon in which bubbles of one-tenth the size or more of the particle size of the detergent particles are released in a case where the detergent particles are dissolved in water. On the other hand, in the conventional compact detergent particles, most of the bubbles formed are the size of less than one-tenth the size of the detergent particles, so that the particles themselves do not undergo self-breakdown. Therefore, sufficiently high-speed dissolution cannot be obtained for these conventional compact detergent particles as in the

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case of the detergent particles of the present invention.

The detergent particles of the present invention having high-speed dissolution by releasing bubbles described above are not limited to specified ones as to
5 their shapes and structures as long as they have given bubble-releasable pores within the particles. For instance, they may be uni-core detergent particles which are explained in the following section, or they may be other detergent particles than the uni-core detergent
10 particles.

An analyzing method of releasing bubbles can be exemplified as follows. An average particle size (median size) based on weight of the detergent particles is previously determined by the use of a measuring device
15 comprising sieves, a sieve-opening of each sieve being from top to bottom 2000 μm , 1410 μm , 1000 μm , 710 μm , 500 μm , 355 μm , 250 μm , 180 μm , and 125 μm , and a receiver. Thereafter, the detergent particles classified between two sieves sandwiching the average particle size
20 are taken out to be used as test samples.

A double-sided adhesive tape is attached to a bottom center of a glass petri dish having an inner diameter of 50 mm. Several classified detergent particles arbitrarily selected from the test samples are adhered to the
25 double-sided adhesive tape in an interval of particles of

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500 μm or so. First, an equivalent diameter (α μm) for each of the detergent particles is calculated from an image obtained by a digital microscope. Examples of the digital microscope include "VH-6300" manufactured by
5 KEYENCE CORPORATION.

Subsequently, 5 ml of ion-exchanged water at 20°C was poured into the glass petri dish, and the dissolution behavior for the individual particles of the subject measurement is observed. When the bubbles are released
10 from the inner portion of the particles, the equivalent diameter (β μm) of the bubbles is measured from an image of an instant at which the bubbles are detached from the particles. Incidentally, in a case where a plurality of bubbles are released from the inner portion of the
15 particles, " β μm " is referred to a maximum value of the equivalent diameter measured for each of the bubbles. The ratio of the bubble diameter to the particle size, i.e. β/α , for each of the particles is calculated.

As described above, a preferred example of a
20 structure of the detergent particles for imparting high-speed dissolution while showing a self-breakdown behavior upon the release of the bubbles includes a structure having pores in the inner portion of the detergent particles with a size comparable to the particle
25 size.

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Specifically, the preferable detergent particles have pores in the inner portion of the classified detergent particles, the pores having a size of one-tenth to four-fifth, preferably one-fifth to four-fifth, the particle size of the particles, wherein the classified detergent particles are obtained by determining an average particle size (median size) based on weight of the detergent particles by the use of a measuring device comprising the sieves described above.

10 The size of the pores can be measured as follows.

 The classified particles are collected, and particles are arbitrarily selected therefrom. The selected particles are split into a half without crashing the particles with a surgical knife, or the like. The split cross section is observed by a scanning electron microscope (SEM). In a case where the equivalent diameter (particle size), i.e. γ μm , of a split cross section of the split particles and the presence of the pores in the inner portion of the particles are confirmed, an equivalent diameter of the pores (pore size), i.e. δ μm , is measured. Incidentally, in a case where a plurality of pores are confirmed, the equivalent diameter δ μm is defined as the largest pore size among them. Thereafter, the ratio of the pore size to the particle size, δ/γ , is calculated.

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The detergent particles are preferably uni-core detergent particles, from the viewpoint of dramatically increasing the dissolution speed.

5 In addition, as to the base particles, in a case where base particles classified in the same manner as those for the uni-core detergent particles are obtained, the preferable base particles have a structure of having pores in the inner portion of the classified base particles, the pores having a size of one-tenth to four-
10 fifth, preferably one-fifth to four-fifth, the particle size of the particles. The size of the pores can be measured in the same manner as that for measurement of the above detergent particles.

15 1.2 High-Speed Dissolution by Localized Structure of Base Particle

In the detergent particles of the present invention, apart from having the dissolution mechanism by releasing bubbles mentioned above, or in combination with the
20 dissolution mechanism, high-speed dissolution from the granular surface can be observed. The features of the present invention reside in that the detergent particles comprise a base particle comprising a water-insoluble inorganic compound, a water-soluble polymer and a water-
25 soluble salt, and a surfactant supported by the base

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particle, wherein the base particle has such a localized structure (hereinafter simply referred to as "localized property of the base particle") that a larger portion of the water-soluble polymer and the water-soluble salt is present near the surface of the base particles rather than in the inner portion thereof. The base particles having a localized property in which a larger portion of the water-soluble substances is present near the surface can exhibit high-speed dissolution because the water-soluble components near the surface are more quickly dissolved in water, thereby showing a dissolution behavior in which the breakdown of the detergent particles from the granular surface is markedly accelerated. Incidentally, the most preferable embodiment for exhibiting high-speed dissolution is detergent particles not only having the localized property described above but also containing given pores within the detergent particles which can release bubbles of given sizes described above. In this case, the high-speed dissolution can be achieved as long as the detergent particles have the above-described localized property in the embodiment of the uni-core detergent particles as well as the embodiment in which the base particles having the uni-core property are aggregated (hereinafter referred to as "multi-core detergent particles"). Incidentally, the definition of the uni-core

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detergent particle will be given in Section 4. described below. Also, the confirmation of the localized property of the base particles will be given in Section 3. described below.

5

2. Composition of Base Particles

The base particles constituting the detergent particles of the present invention comprise as main components (A) a water-insoluble inorganic compound, (B) a
10 water-soluble polymer, and (C) a water-soluble salt.

As the water-insoluble inorganic compound of (A) Component, those having a primary average particle size of from 0.1 to 20 μm are preferable. Examples thereof include crystalline or amorphous aluminosilicates; clay
15 compounds such as silicon dioxide, hydrated silicate compounds, perlite, and bentonite, among which crystalline or amorphous aluminosilicates, silicon dioxide and hydrated silicate compounds are favorably used. In particular, the crystalline aluminosilicates are
20 preferable because they act as a metal ion capturing agent in the detergent composition.

The primary (average) particle size of the crystalline aluminosilicate used herein is preferably from about 0.1 to about 2.0 μm , and smaller the primary
25 particle size, more preferable, from the viewpoints of the

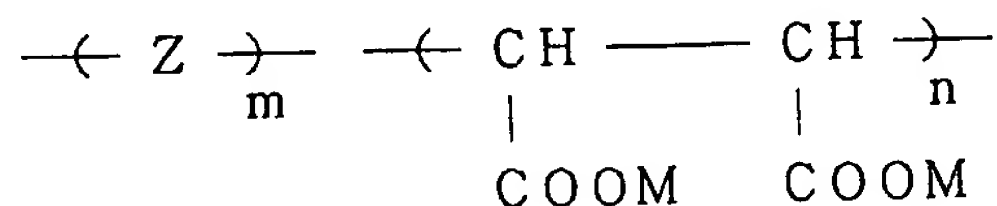
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cationic exchange speed and exhibition of the oil-
 absorbing ability of the base particles described below.
 The particle size can be confirmed by a scanning electron
 microscope. Also, aggregates of the primary particles can
 5 be used.

As the water-soluble polymer of (B) Component, there
 can be cited carboxylic acid-based polymers, carboxymethyl
 cellulose, water-soluble starches and sugars, among which
 the carboxylic acid-based polymers are preferable from the
 10 viewpoint of detergency.

Besides the function of capturing the metal ions, the
 carboxylic acid-based polymers have the function of
 dispersing the solid particle stains from clothes to
 washing water and the function of preventing re-deposition
 15 (re-staining) of the particles to the clothes. For these
 purposes, it is preferable to include carboxylic acid-
 based polymers such as a copolymer having a molecular
 weight of about several thousands to about 100,000 and
 represented by the following formula (I):

20



wherein Z is an olefin having 1 to 8 carbon atoms, acrylic
 25 acid, methacrylic acid, itaconic acid, methallylsulfonic

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acid, or the like, which is a monomer copolymerizable with maleic acid (anhydride) or a maleate; m and n take such values that a molecular weight of the copolymer is several hundred to 100,000; and M is Na, K, NH₄, amine, or H;

5 and/or

a homopolymer having a molecular weight of about several thousands to about 100,000 represented by the formula (II):



wherein p is a homopolymerizable monomer, exemplified by acrylic acid, methacrylic acid, maleic acid, or the like; q takes a value such that the molecular weight of the resulting homopolymer is from several hundred to 100,000, the homopolymer being in the form of an Na salt, a K salt, or an NH₄ salt.

Incidentally, the copolymer is generally prepared by random polymerization.

Among these carboxylic acid-based polymers, the salts of acrylic acid-maleic acid copolymers and the salts of polyacrylic acids are particularly excellent, wherein the salts are Na, K, or NH₄ salts. The molecular weight is appropriately from 1,000 to 80,000. The carboxylic acid-based polymers can be usually easily prepared by polymerizing unsaturated organic carboxylic acids or

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organic polycarboxylic acids, and the resulting polymers having a molecular weight of 2,000 or more and a number of carboxyl groups of 10 or more are preferable.

Besides the above carboxylic acid-based polymers,
5 polymers such as polyglycidyl acid salt or the like;
cellulose derivatives such as carboxymethyl cellulose;
aminocarboxylic acid-based polymers such as polyaspartates
also have metal ion capturing ability, dispersing ability,
and re-deposition preventing ability.

10 The amount of each of the copolymer of the formula
(I) and/or the homopolymer of the formula (II) is
preferably from 1 to 20% by weight, more preferably from 2
to 10% by weight in the detergent composition.

As the water-solution salt of (C) Component, there
15 can be included water-soluble inorganic salts typically
exemplified by alkali metal salts, ammonium salts or amine
salts of radicals such as carbonate, hydrogencarbonate,
sulfate, sulfite, hydrogensulfate, phosphate, halide, or
the like; and water-soluble organic acid salts having low-
20 molecular weights such as citrates, fumarates, and the
like. Among them, the inorganic salts each having
carbonate radical, sulfate radical, and sulfite radical
are preferable. The inorganic salts are preferable
because the pores from the detergent particles are further
25 thermally expanded by causing hydration heat and

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dissolution heat by the reaction with water, thereby accelerating the self-breakdown of the particles.

Here, sodium carbonate is preferably used as an alkalizing agent showing a suitable pH buffer region in the washing liquid. The alkalizing agents other than sodium carbonate are amorphous or crystalline silicates. The amorphous silicate (water glass) has been widely used as an alkalizing agent as detergent starting materials. In a case where the aluminosilicate is used as a water-insoluble inorganic compound of the base particles, when the amorphous silicate (water glass) is included in the composition, hardly soluble, insoluble mass is likely to be formed, so that much care must be attended for the kinds and the amounts of the base materials.

The salts having high degree of dissociation, such as sodium sulfate, potassium sulfate, and sodium sulfite, have increased ionic strength of the washing liquid, thereby favorably acting against sebum stains, and the like. In addition, the sulfite radical is important in having the effects of reducing hypochlorite ions contained in tap water, thereby having an effect of preventing oxidation degradation of the detergent components such as enzymes and perfumes by the hypochlorite ions. Also, the use of sodium tripolyphosphate, which is a builder having excellent metal ion capturing ability and alkalizing

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ability, does not hinder the effects of the present invention. In addition, as the water-soluble organic salts having a low molecular weight, those base materials having a large $pKCa^{2+}$ and/or having a large cationic exchange capacity are preferable with expectation of imparting good metal ion capturing ability. Besides the citrates, there can be also included methyliminodiacetates, iminodisuccinates, ethylenediaminedisuccinates, taurine diacetates, hydroxyethyliminodiacetates, β -alanine diacetate, hydroxyiminodisuccinates, methylglycine diacetate, glutamic acid diacetate, asparagine diacetate, serine diacetate, and the like. Here, from the viewpoint of detergency, taurine diacetates, hydroxyethyliminodiacetates, β -alanine diacetate, hydroxyiminodisuccinates, methylglycine diacetate, glutamic acid diacetate, asparagine diacetate, serine diacetate are preferable.

In addition, when anions other than carbonate radical, such as sulfate radical and sulfite radical, and cations other than sodium ions, such as potassium ions and ammonium ions, are mixed in the base particles, there is an effect in the anti-caking property. Also, similar effects can be also exhibited when adding an anionic surfactant such as an alkylbenzenesulfonate in an amount

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of 5 to 25% by weight.

The composition of the base particles is as follows.
The water-insoluble inorganic compound of Component (A) is preferably from 20 to 90% by weight, more preferably from 30 to 75% by weight, still more preferably from 40 to 70% by weight. The water-soluble polymer of Component (B) is preferably from 2 to 30% by weight, more preferably from 3 to 20% by weight, still more preferably from 5 to 20% by weight. The water-soluble salts of Component (C) is preferably from 5 to 78% by weight, more preferably from 10 to 70% by weight, still more preferably from 10 to 67% by weight, more preferably from 20 to 60% by weight, still more preferably from 20 to 55% by weight. Within the above ranges, the base particles are favorable in the aspects of having a structure in which near the surfaces of the base particles is coated with a water-soluble component, so that the coating layer is sufficiently formed on the particle surface, thereby making its particle mechanical strength sufficient. Also, it is preferable from the viewpoint of the dissolution of the resulting detergent composition.

In addition, besides these three components (A) to (C), there may be included in the base particles, surfactants and other supplemental components suitably used in detergent compositions, such as fluorescent dyes,

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pigments and dyes.

In particular, although the surfactant is not an essential component of the base particles, an addition thereof in a slurry prepared in Step (a) of Section 5. described below is preferable because the drying efficiency in Step (b) and the high-speed dissolution property of the resulting detergent particles are improved thereby. The amount of the surfactant in the slurry is preferably 10% by weight or less, more preferably from 1 to 10% by weight, still more preferably from 2 to 8% by weight. Within the above range, sufficient particle mechanical strength can be obtained. Incidentally, the amounts are obtained on the basis of the solid components of the slurry.

Higher the oil-absorbing ability of the base particles, more likely the high-speed dissolution is exhibited even when large amounts of the surfactant are added.

Examples of the factors for improving the oil-absorbing ability of the base particles include use of base materials having a large oil-absorbing ability as the water-insoluble inorganic compounds of Component (A). An example of suitable base material is A-type zeolite from the aspects of the metal ion capturing ability and costs. Here, the A-type zeolite has an oil-absorbing ability

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measured by a method according to JIS K 5101 of from 40 to 50 mL/100 g (Examples thereof include trade name: "TOYOBUILDER," manufactured by Tosoh Corporation.). Besides the above, there can be included P-type (for example, trade names: "Doucil A24" and "ZSE064" manufactured by Crosfield B.V.; oil-absorbing ability: 60 to 150 mL/100 g), and X-type (for example, trade name: "Wessalith XD" manufactured by Degussa-AG; oil-absorbing ability: 80 to 100 mL/100 g). In addition, amorphous silica and amorphous aluminosilicates having high oil-absorbing ability but low metal ion capturing ability can be used as water-insoluble inorganic compounds. Examples thereof include amorphous aluminosilicates disclosed in Japanese Patent Laid-Open No. 62-191417, page 2, lower right column, line 19 to page 5, upper left column, line 17 (particularly, it is preferable that the initial temperature is in the range from 15° to 60°C); amorphous aluminosilicates disclosed in Japanese Patent Laid-Open No. 62-191419, page 2, lower right column, line 20 to page 5, lower left column, line 11 (particularly those having oil-absorbing ability of 170 mL/100 g are preferable); amorphous aluminosilicates disclosed in Japanese Patent Laid-Open No. 9-132794, column 17, line 46 to column 18, line 38, Japanese Patent Laid-Open No. 7-10526, column 3, line 3 to column 5, line 9, Japanese Patent Laid-open No.

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6-227811, column 2, line 15 to column 5, line 2, and Japanese Patent Laid-Open No. 8-119622, column 2, line 18 to column 3, line 47 (oil-absorbing ability: 285 mL/100 g). For example, there can be used as an oil-absorbing carrier, "TOKSIL NR" (manufactured by Tokuyama Soda Co., Ltd.; oil-absorbing ability: 210 to 270 mL/100 g); "FLORITE" (manufactured by Tokuyama Soda Co., Ltd.; oil-absorbing ability: 400 to 600 mL/100 g); "TIXOLEX 25" (manufactured by Kofran Chemical; oil-absorbing ability: 220 to 270 mL/100 g); "SILOPURE" (manufactured by Fuji Devison Co., Ltd.; oil-absorbing ability: 240 to 280 mL/100 g), and the like. In particular, the oil-absorbing carriers having properties described in Japanese Patent Laid-Open No. 5-5100, column 4, line 34 to column 6, line 16 (especially, the oil-absorbing carriers described in column 4, line 43 to 49); and Japanese Patent Laid-Open No. 6-179899, column 12, line 12 to column 13, line 17 and column 17, line 34 to column 19, line 17 are favorably used.

In the present invention, those water-insoluble inorganic compounds may be used alone or in combination of several kinds. Among them, from the viewpoint of maintaining, or without deteriorating, high dissolution property even when stored for a long period of time, aluminosilicates having an Si/Al molar ratio of preferably

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4.0 or less, more preferably 3.3 or less.

3. Localized Property of Base Particles

As a method for confirming the localized property of
5 the base particles, there can be employed, for instance, a
combined method of Fourier transformer infrared
spectroscopy (FT-IR) and photoacoustic spectroscopy (PAS)
(simply abbreviated as "FT-IR/PAS"). As described in
"APPLIED SPECTROSCOPY," 47, 1311-1316 (1993)), the
10 distribution state of the substances in the direction of
depth from the surface of the samples can be confirmed by
FT-IR/PAS.

The measurement method for determining the structure
of the base particles of the present invention will be
15 exemplified below.

Each of the cell is charged with base particles of
two different states to conduct FT-IR/PAS measurement, and
the structure of the base particles can be determined by
comparing the measurement values. In other words, one
20 FT-IR/PAS measurement is taken for the base particles in a
state where the original structure thereof is retained,
and another FT-IR/PAS measurement is taken for the base
particles in a uniform state by sufficiently pulverizing
the base particles with an agate mortar. The FT-IR/PAS is
25 measured, for instance, by using an infrared spectrometer

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"FTS-60A/896" (manufactured by Bio-Rad Laboratories), and the PAS accessory includes an acoustic detector "Model 300" manufactured by MTEC Corporation. The measurement conditions are resolution of 8 cm^{-1} , scanning speed of 5 0.63 cm/s , and 128 scans. In the above measurement conditions, the information up to a depth of about $10\text{ }\mu\text{m}$ from the surface of the base particles is included. In the PAS spectra of the base particles, each of the characteristic peaks of sodium carbonate, sodium sulfate, 10 zeolite and sodium polyacrylate can be read off at 1434 cm^{-1} (CO_3^{2-} degenerate stretching vibration), 1149 cm^{-1} (SO_4^{2-} degenerate stretching vibration), 1009 cm^{-1} (Si-O-Si anti-symmetric stretching vibration), and 1576 cm^{-1} (CO_2^- anti-symmetric stretching vibration), respectively, and the 15 areal intensity of each peak is measured. The relative areal intensity of each of the characteristic peaks of the water-soluble salt such as sodium carbonate or sodium sulfate to the characteristic peaks of the zeolite, when measured for each of the state in which the structure of 20 the base particles is retained, and the state in which the base particles are uniformly pulverized, is obtained. The resulting relative intensity is then compared with the relative areal intensity of the characteristic peaks of the water-soluble polymer to the characteristic peaks of 25 the zeolite, when measured for each of the above states,

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the structural features of the base particles can be determined. Concretely, the base particles have a localized property such that larger portions of the water-soluble polymer and the water-soluble salt are included near the surface of the base particles than the inner portion thereof, and that a larger portion of the water-insoluble inorganic compound is included in the inner portion of the base particles than near the surface thereof. In the base particles of the present invention, the relative areal intensity of the water-soluble salt to the zeolite and the relative areal intensity of the water-soluble polymer to the zeolite, when measured in a state in which the structure has localized property of the above components, are higher than each of the relative areal intensity when measured in the state in which the base particles are pulverized to give a uniform state.

With respect to the base particles of the present invention, ratios of the relative areal intensity of the characteristic peaks of the water-soluble salts and the water-soluble polymer to the characteristic peaks of the zeolite when measured in the state in which the localizing structure of the components is retained to the relative areal intensity of the characteristic peaks when measured in the state in which the base particles are pulverized to give a uniform state are calculated. As to the water-

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soluble salts, the ratio is 1.1 or more, preferably 1.3 or more, and as to the water-soluble polymer, the ratio is 1.3 or more, preferably 1.5 or more. When the base particles have these ratios of relative areal intensities, the base particles can be said to have a localized structure.

In other words, the structural features of the base particles of the present invention in which the contents of the water-soluble salts such as sodium carbonate and sodium sulfate and the water-soluble polymer such as sodium polyacrylate are relatively larger in a portion near the surface of the base particles, and the content of the water-insoluble inorganic compound such as zeolite is relatively larger in the inner portion of the base particles can be confirmed by the measurement of FT-IR/PAS.

The base particles of the present invention retaining the original state and in a uniformly ground state are measured by FT-IR/PAS, and the results standardized with the peak intensity of the zeolite are shown in Figure 1, wherein the solid line indicates the results for the base particles retaining the original structure, and the dotted line indicates the results for the base particles in a uniformly ground structure. It is clear from Figure 1 that the relative areal intensity of sodium carbonate and

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sodium sulfate to the zeolite and the relative areal intensity of sodium polyacrylate to the zeolite, when measured in the state in which the base particles retain the original structure, are higher than each of the
5 relative areal intensity when measured in the state in which the base particles are pulverized to give a uniform state. Incidentally, as the base particles illustrated in Figure 1, Base Particles 1 of the inventive product described in Examples set forth below are used.

10 As other examples of the method of structural analysis of the base particles, there can be employed energy dispersion-type X-ray spectroscopy (EDS) and electron probe microanalysis (EPMA). These analysis methods can analyze two-dimensional distribution of
15 elements by scanning the sample surface with an electron beam.

For instance, as the energy dispersion-type X-ray diffractometer, there can be employed "EMAX 3770" manufactured by Horiba, LTD. which is attached to SEM such
20 as an electric field-irradiating scanning electron microscope "Model S-4000," manufactured by Hitachi, Ltd. In the case where the water-soluble salt, the water-insoluble inorganic compound, and the water-soluble polymer are contained in the base particles of the present
25 invention, the distribution state of elements measured

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with respect to C, O, Na, Al, Si, S, and the like of the split cross section of the base particles obtained by stiffening the base particles with a resin and splitting the stiffened particles with a microtome, is such that Na
5 and S are present in large amounts in the outer side of the particle cross section, and that Al and Si are present in large amounts in the central portion. Therefore, there can be confirmed that the structure of the base particles of the present invention in which large amounts of the
10 water-soluble salts are included near the surface of the base particles and a large amount of the water-insoluble inorganic compound is included in the central portion.

Figures 2 to 6 each shows an SEM image of the base particles of the present invention and an EDS measurement
15 result for Na, Al, Si and S. Incidentally, the illustrated base particles are Base Particles 1 of Examples.

It is clear from Figures 3 to 6 that in the base particles of the present invention, large proportions of
20 Na and S, the characteristic constituting elements for sodium carbonate and sodium sulfate, which are the water-soluble salts, are found near the surface of the particle (near the outer peripheral surface in the particle cross section), and that large proportions of Al and Si, the
25 characteristic constituting elements of zeolite, which are

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the water-insoluble inorganic compound, are found in the central portion of the particle. In Figures 3 to 6, portions containing large proportions of each of these elements have high brightness.

5

4. Base Particles and Uni-Core Detergent Particles

It is preferable that the detergent particles of the present invention are uni-core detergent particles from the viewpoint of high-speed dissolution. The term

10 "uni-core detergent particles" used in the present invention refers to detergent particles each prepared by using one base particle as a nucleus, wherein a single detergent particle has one base particle as a nucleus.

As a factor for expressing the uni-core property, the

15 degree of particle growth as defined in Equation (2):

$$\begin{array}{lcl} \text{Degree of} & & \text{Average Particle Size of} \\ \text{Particle} & = & \text{Final Detergent Particles} \\ \text{Growth} & & \hline & & \text{Average Particle Size of} \\ & & \text{Base Particles} \end{array} \quad (2)$$

20

can be employed. The degree of particle growth is preferably 1.5 or less, more preferably 1.3 or less.

25 The term "average particle size of final detergent particles" refers to an average particle size of the detergent particles obtained by supporting a surfactant by a base particle, or an average particle size of the

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detergent particles in which the detergent particles supporting a surfactant are subjected to surface improvement treatment.

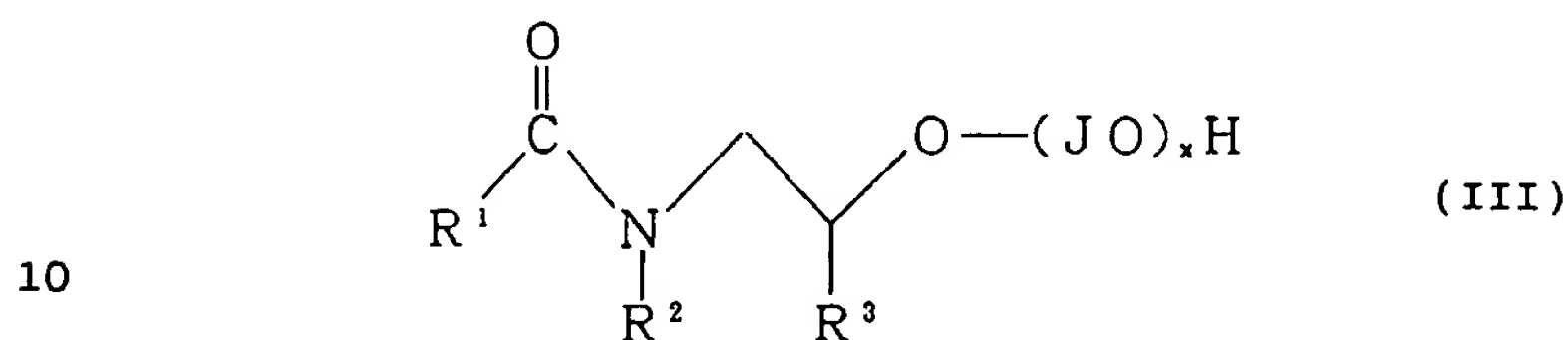
In the present invention, the surfactant to be supported by the base particle may be one or a combination of anionic surfactants, nonionic surfactants, amphoteric surfactants, and cationic surfactants, with a preference given to one or a combination of an anionic surfactant and a nonionic surfactant.

The anionic surfactant is preferably salts of esters obtained from an alcohol having 10 to 18 carbon atoms and sulfuric acid; salts of esters obtained from an alkoxyated product of an alcohol having 8 to 20 carbon atoms and sulfuric acid; alkylbenzenesulfonates; paraffinsulfonates; α -olefinsulfonates; salts of α -sulfonated fatty acids; salts of alkyl esters of α -sulfonated fatty acids; and salts of fatty acids. Particularly in the present invention, it is preferable that the linear alkylbenzenesulfonates of which an alkyl moiety has 10 to 14 carbon atoms, more preferably 12 to 14 carbon atoms. As the counter ions, a preference is given to the alkali metals and amines, and particularly sodium and/or potassium, monoethanolamine, and diethanolamine are preferable.

Preferable examples of the nonionic surfactant

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include preferably polyoxyalkylene alkyl ethers, alkylene
 polyglycosides, polyoxyalkylene alkylphenyl ethers,
 polyoxyalkylene sorbitan fatty acid esters,
 polyoxyalkylene glycol fatty acid esters, polyoxyethylene
 5 polyoxypropylene block polymers, and polyoxyalkylene
 alkylolamides represented by the following formula (III):



wherein R^1 is a saturated or unsaturated hydrocarbon group
 having an average number of carbon atoms of 7 to 19; each
 of R^2 and R^3 is independently hydrogen atom or methyl
 15 group; JO is an oxyalkylene group, which is oxyethylene
 group, oxypropylene group, or a mixture thereof; x is an
 average additional molar number of the oxyalkylene group,
 wherein x satisfies $0.5 \leq x \leq 10$.

Particularly, the polyoxyalkylene alkyl ether
 20 preparing by adding an alkylene oxide such as ethylene
 oxide or propylene oxide to an alcohol having 10 to 18
 carbon atoms in an amount of 4 to 20 moles is preferable
 as the nonionic surfactant, wherein the resulting
 polyoxyalkylene alkyl ether has an HLB value as calculated
 25 by Griffin method of from 10.5 to 15.0, preferably from

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11.0 to 14.5. Also preferable as the nonionic surfactant is a polyoxyalkylene alkylolamide represented by the formula (III), where R^1 is a saturated hydrocarbon group having an average number of carbon atoms 11 to 13, each of
5 R^2 and R^3 is hydrogen atom, and x satisfies $1 \leq x \leq 5$.

The amount of the surfactant supported by the base particle of the present invention is preferably from 5 to 80 parts by weight, more preferably from 5 to 60 parts by weight, still more preferably from 10 to 60 parts by
10 weight, still more preferably from 20 to 60 parts by weight, based on 100 parts by weight of the base particles, from the viewpoint of exhibiting detergency. Here, the supporting amount of the anionic surfactant is preferably from 1 to 60 parts by weight, more preferably
15 from 1 to 50 parts by weight, still more preferably from 3 to 40 parts by weight. The supporting amount of the nonionic surfactant is preferably from 1 to 45 parts by weight, more preferably from 1 to 35 parts by weight, still more preferably from 4 to 25 parts by weight. The
20 anionic surfactant and the nonionic surfactant can be used alone, or they can be preferably used as a mixture. In addition, the amphoteric surfactant or the cationic surfactant may be also used according to its purpose. The term "supporting amount of the surfactant" used herein
25 does not include the amount of the surfactant added when a

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surfactant is added in the preparation of slurry in Step (a) of Section 5.1 described below.

The favorable properties for the base particles obtained in the present invention are as follows.

5

4.1 Properties of Base Particles

4.1.1 Bulk density: from 400 to 1,000 g/liter, preferably from 500 to 800 g/liter. The bulk density is measured by a method according to JIS K 3362. In the
10 above range, the detergent particles having a bulk density of 500 g/liter or more and good high-speed dissolution can be obtained.

4.1.2 Average particle size: from 150 to 500 μm , preferably from 180 to 300 μm . The average particle size,
15 calculated as a median size, is measured by vibrating each of standard sieves according to JIS Z 8801 for 5 minutes, and calculating a weight percentage depending upon the size openings of the sieves.

4.1.3 Particle mechanical strength: Ranging from 50 to
20 2,000 kg/cm^2 , preferably from 100 to 1,500 kg/cm^2 , more preferably from 150 to 1,000 kg/cm^2 . In the above range, the base particles show good breakdown property, so that the detergent particles having excellent high-speed dissolution can be obtained.

25 The particle mechanical strength is measured by the

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following method.

A cylindrical vessel of an inner diameter of 3 cm and a height of 8 cm is charged with 20 g of a sample, and the sample-containing vessel is tapped for 30 times. The sample height (an initial sample height) after tapping is measured. Thereafter, an entire upper surface of the sample kept in the vessel is pressed at a rate of 10 mm/min with a pressing machine to take measurements for a load-displacement curve. The particle mechanical strength (S) is defined according to the present equation:

$$S = \frac{X \cdot Y}{Z}$$

wherein X is a slope of the linear portion at a displacement rate of 5% or less;
Y is an initial sample height; and
Z is a pressed area.

4.1.4 Oil-absorbing ability: 20 ml/100 g or more, preferably 40 ml/100 g or more. In the above range, the aggregation of the base particles can be suppressed, so that the uni-core property of the detergent particles can be favorably maintained.

The oil-absorbing ability is measured by the following method.

A cylindrical mixing vessel of an inner diameter of about 5 cm and a height of about 15 cm which is equipped

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with agitation impellers in the inner portion thereof is charged with 100 g of a sample. With stirring the contents at 350 rpm, linseed oil is supplied at a rate of about 10 ml/min at 25°C. The oil-absorbing ability is defined as an amount of linseed oil supplied when the agitation motor reaches the highest level.

4.1.5 Water content: The water content is 20% by weight or less, preferably 10% by weight or less, more preferably 5% by weight or less. In this range, the base particles having excellent properties can be obtained.

The water content is measured by the following method.

A three-gram sample is placed on a weighing dish, and the sample is dried with an electric dryer at 105°C for 2 hours. The weight of the sample after drying is measured. The water content is determined by the weight loss, namely the difference of the sample before and after drying, and the water content is expressed in percentage.

4.2 Properties of Uni-Core Detergent Particles

4.2.1 Uni-Core Property

A preferred embodiment of the detergent particles of the present invention is uni-core detergent particles in which each detergent particle comprises a single base particle as a core. A method for confirming the uni-core

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property of the detergent particles described above is exemplified as follows. The uni-core property of the detergent particles can be confirmed by splitting some detergent particles arbitrarily sampled from the detergent particles of a size near its average particle size, and observing presence or absence of the base particles in the detergent particles and a number of cores which are present in the inner portion of the particles by a scanning electron microscope (SEM). Further, the uni-core property of the detergent particles can be also confirmed by detecting a two-dimensional elementary distribution of the split cross section of the detergent particles stiffened by the resin by EDS or EPMA.

Figure 7 is an example of confirmation of the uni-core property of the detergent particles made by an SEM observation. Incidentally, the SEM photograph exemplified in Figure 7 is an SEM image observed on the split cross section of the detergent particles prepared from Base Particles 1 of the present invention described in Examples which are set forth below. It is clear from Figure 7 that the detergent particles of the present invention are uni-core detergent particles each comprising one base particle as a core.

In addition, as a method for distinguishing the aggregated particles by a substance soluble to an organic

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solvent such as ethanol, for example, a surfactant, and the uni-core detergent particles, there can be cited a method of confirming a degree of changes in the particle sizes before and after extraction of an organic solvent-soluble component. Incidentally, the kinds of the organic solvent used for extraction can be appropriately selected by the kinds of the binder substance which binds each constituting unit of the detergent particles. Further, the presence or absence of the base particles can be also confirmed by making an SEM observation of an organic solvent-insoluble component after extraction procedure of the binder substance by using an appropriate organic solvent.

A method of confirming the uni-core property by solvent extraction is exemplified below.

A one-hour reflux operation of 15 g of a detergent sample-reduced and weighed is carried out with 30 ml of 95%-ethanol heated in a water bath. Thereafter, an ethanol-insoluble component is gradually separated by suction filtration while sufficiently washing with hot ethanol. The separated ethanol-insoluble component is dried under reduced pressure for 24 hours, and the dried insoluble component is collected so as not to break the particle structure of the ethanol-insoluble component. Similar operations as above are repeated for another

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weighed detergents several times to obtain 100 g of an ethanol-insoluble component. The average particle size of the resulting ethanol-insoluble component is measured by vibrating each of standard sieves according to JIS Z 8801
5 for 5 minutes, and calculating a weight percentage depending upon the size openings of the sieves. Further, the particles classified by each sieve opening as occasion demands are observed by SEM to confirm whether or not the particles are the base particles of the present invention
10 and to confirm the presence or absence of an ethanol-insoluble component added in the subsequent steps. In the case where the presence of an ethanol-insoluble component added in the subsequent steps other than the base particles is confirmed in the ethanol-insoluble component,
15 the average particle size of the base particles is obtained after reducing their affects to the particle size distribution on the ethanol-insoluble components added in the subsequent steps, thereby adjusting an average particle size of the ethanol-insoluble component. The
20 uni-core property of the detergent can be confirmed by comparing the average particle size of the base particles and the average particle size of the obtained untreated sample detergent. In other words, the solvent-insoluble component is collected by separation procedure using an
25 appropriately selected solvent or a combination of such

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solvents, and in a case where additives of the subsequent steps are present, the solvent-insoluble component is collected by removing the affects of the additives. The uni-core detergent particles in the present invention
5 satisfy the relationship of Y/X of 1.5 or less, preferably 1.3 or less, wherein X (μm) is an average particle size of the solvent-insoluble component obtained, which is nearly the same as an average particle size of the base particles, and Y (μm) is an average particle size of the
10 untreated sample detergent.

4.2.2 High-Speed Dissolution

The uni-core detergent particles of the present invention have high-speed dissolution. In the present invention, the high-speed dissolution of the uni-core
15 detergent particles can be evaluated by 60-seconds dissolution rate or 30-seconds dissolution rate. In the present invention, as long as either dissolution rate for the uni-core detergent particles satisfies a given range, such uni-core detergent particles reveal high-speed
20 dissolution.

The term "high-speed dissolution" in 60-seconds dissolution rate of the uni-core detergent particles as defined by the present invention refers to a dissolution rate of the detergent particles as calculated by the
25 following method is 90% or more. The dissolution rate is

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preferably 94% or more, more preferably 97% or more.

The test stirring conditions described above are more specifically detailed below. A one-liter beaker, which has a cylindrical form having an inner diameter of 105 mm and a height of 150 mm (for instance, a one-liter glass beaker manufactured by Iwaki Glass Co., Ltd.), is charged with one-liter of hard water cooled to 5°C and having a water hardness corresponding to 71.2 mg CaCO₃/liter, wherein a molar ratio of Ca/Mg is 7/3. With keeping the water temperature constant at 5°C with a water bath, water is stirred with a stirring bar of 35 mm in length and 8 mm in diameter (for instance, Model "TEFLON SA" manufactured by ADVANTEC) at a rotational speed of 800 rpm, wherein a depth of swirling to the water depth is about 1/3. The detergent particles accurately being sample-reduced and weighed so as to be 1.0000 ± 0.0010 g are supplied and dispersed in water with stirring, and stirring is continued. After 60 seconds from supplying the detergent particles, a liquid dispersion of the detergent particles in the beaker is filtered with a standard sieve of 100 mm in diameter and a sieve-opening of 74 μm as defined by JIS Z 8801 of a known weight. Thereafter, water-containing detergent particles remaining on the sieve are collected in an open vessel of a known weight together with the sieve. Incidentally, the operation time from the start of

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filtration to collection with the sieve is set at 10 sec \pm
2 sec. The remaining insolubles of the collected
detergent particles are dried for one hour in an electric
dryer heated to 105°C. Thereafter, the dried insolubles
5 are cooled by keeping in a desiccator containing a silica
gel therein at 25°C for 30 minutes. After cooling the
remaining product, a total weight of the dried remaining
product of the detergent, the sieve and the collected
vessel is measured, and the dissolution rate (%) is
10 calculated by Equation (1).

The term "high-speed dissolution" in 30-seconds
dissolution rate of the uni-core detergent particles as
defined by the present invention refers to a dissolution
rate of the detergent particles of 82% or more, as
15 calculated by a similar method as the method of
calculating 60-seconds dissolution rate except that a
liquid dispersion of the detergent particles is filtered
after 30 seconds from supplying the detergent particles.
The dissolution rate is preferably 85% or more, more
20 preferably 90% or more.

Even in the above evaluation method using a
low-temperature water wherein the dissolution rate of the
detergent is drastically lowered, the uni-core detergent
particles in the present invention each of which comprises
25 the base particles have the high dissolution rate

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mentioned above, thereby showing an extremely high high-speed dissolution property notably distinguishable from the dissolution property of conventional detergents. The uni-core detergent particles of the present invention
5 having excellent dissolution property as described above not only have an effect of improving detergency by more speedily releasing the deterging components into a wash tub, but also have major advantages in quality in which there are no remaining insolubles of detergents even when
10 washing in a short period of time or with low mechanical strength such as a hand-washing cycle, a gentle cycle, and a quick cycle employed in fully automatic washing machines used today.

The favorable properties for the uni-core detergent
15 particles obtained in the present invention are as follows.

4.2.3 Bulk density: 500 g/liter or more, preferably from 500 to 1,000 g/liter, more preferably from 600 to
20 1,000 g/liter, still more preferably from 650 to 850 g/liter. The bulk density is measured by a method according to JIS K 3362.

4.2.4 Average particle size: from 150 to 500 μm , preferably from 180 to 300 μm . The average particle size,
25 calculated as a median size, is measured by vibrating each

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of standard sieves according to JIS Z 8801 for 5 minutes, and calculating a weight percentage depending upon the size openings of the sieves.

4.2.5 Flowability: evaluated as flow time of preferably
5 10 seconds or shorter, more preferably 8 seconds or shorter. The flow time is a time period required for dropping 100 ml of powder from a hopper used in a measurement of bulk density according to JIS K 3362.

4.2.6 Caking property: evaluated by sieve permeability
10 of preferably 90% or more, more preferably 95% or more.

The testing method for caking property is as follows.
A lidless box having dimensions of 10.2 cm in length, 6.2 cm in width, and 4 cm in height is made out of a filter paper (No. 2, manufactured by ADVANTEC) by stapling
15 the filter paper at four corners. A 50 g sample is placed in this box, and an acrylic resin plate with a weight of 15 g and a lead plate (or an iron plate) with a weight of 250 g are placed on the sample. The above box is maintained in a thermostat kept at a constant humidity
20 under conditions of a temperature of 30°C and a humidity of 80%, the caking conditions after 7 days and after one month are evaluated by calculating the permeability as explained below.

[Permeability]

25 A sample obtained after the above testing is gently

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placed on a sieve with a sieve opening of 4760 μm
according to JIS Z 8801, and the weight of the powder
passing through the sieve is measured. The permeability,
based on the sample obtained after the above testing is
5 calculated by the following equation:

$$\begin{aligned} &\text{Permeability (\%)} \\ &= \frac{\text{Weight of Powder Passing Through Sieve (g)}}{\text{Weight of Entire Sample (g)}} \times 100 \end{aligned}$$

10

4.2.7 Exudation property: determined by gross
15 examination of preferably two ranks or better, more
preferably 1 rank. In the above range of ranks, it is
preferable because the adhesion of the powder containing a
nonionic surfactant to equipments during transportation
can be prevented, and no additional procedure of
20 preventing exudation property to the vessel would be
necessitated.

The testing method for exudation property is as
follows. The exudation property is evaluated by a gross
examination of exudation conditions of a surfactant at a
25 bottom portion of the box obtained after the caking test,
the examination being made from a side where the powder is
not contacted therewith. The evaluation for exudation
property is made based on the area of wetted portion

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occupying the bottom portion of the box in 1 to 5 ranks.

Each of the ranks is determined as follows:

- Rank 1: Not wetted.
- 2: About one-quarter of the bottom area being
5 wetted.
- 3: About one-half the bottom area being
wetted.
- 4: About three-quarter of the bottom area
being wetted.
- 10 5: The entire bottom area being wetted.

5. Method for Preparing Uni-Core Detergent Particles

The uni-core detergent particles of the present
invention can be prepared by a method including the
15 following Step (a) to Step (c).

Step (a): preparing a slurry containing a water-insoluble
inorganic compound, a water-soluble polymer, and
a water-soluble salt, wherein 60% by weight or
more of water-soluble components comprising the
20 water-soluble polymer and the water-soluble salt
is dissolved in the slurry;

Step (b): spray-drying the slurry obtained in Step (a) to
prepare base particles containing a
water-insoluble inorganic compound, a
25 water-soluble polymer, and a water-soluble salt;

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and

Step (c): adding a surfactant to the base particles
obtained in Step (b) to support the surfactant
thereby.

5

Moreover, in order to further improve the properties
and quality of the resulting detergent particles, it is
preferable to further add a surface-modifying step
subsequent to Step (c). Preferred embodiments for each of
10 Steps (a) to (c) and a surface-modifying step will be
described below.

5.1 Step (a) (Step for Preparation of Slurry)

Step (a) comprises preparing a slurry in order to
15 prepare base particles. The slurry usable in the present
invention may be preferably a non-curable slurry which can
be conveyed with a pump. Also, the addition method of the
components and their order can be appropriately varied
depending upon the production conditions. It is
20 preferable that the content of the water-insoluble
component (A) in the slurry is from 6 to 63% by weight,
and the content of the water-soluble components (B,C) in
the slurry is from 2.1 to 56% by weight.

In order that the base particles obtainable in Step
25 (b) have the structure in the present invention, that is

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the structure having localized property of components in which larger amounts of the water-soluble components (B, C) are present near the surface of the base particles than the inner portion thereof, and larger amounts of the water-insoluble component (A) are present in the inner portion of the base particles than near the surface thereof, the water-soluble components (B, C) in Step (b) are required to be shifted to the granular surface along with evaporation of moisture. In order to satisfy this requirement, the dissolution rate of the water-soluble components (B, C) in the slurry becomes an important factor. In other words, it is required to prepare a slurry in which the water-soluble components (B, C) are dissolved in an amount of 60% by weight or more, preferably 70% by weight or more, more preferably 85% by weight or more, still more preferably 90% by weight or more. In general, the water content required for preparing such a slurry is preferably from 30 to 70% by weight, more preferably from 35 to 60% by weight, still more preferably from 40 to 55% by weight. The water content is desirably higher than the lower limit of the above range, so that the water-soluble components (B, C) can be sufficiently dissolved in the slurry, and thereby the proportions of the water-soluble components (B, C) which are present near the surface of the resulting base

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particles are increased. In addition, the water content is desirably lower than the upper limit of the above range, so that the water content needed to be evaporated in Step (b) can be well controlled, thereby giving high productivity.

The measurement method of the dissolution rate of the water-soluble components (water-soluble polymer and water-soluble salt) in the slurry is as follows. The slurry is filtered under reduced pressure, and the water concentration P (%) in the filtrate is measured. The water content of the slurry is denoted as Q (%); and the concentration of the water-soluble components in the slurry is denoted as R (%). The dissolution rate of the water-soluble components is calculated by Equation (3):

$$\text{Dissolution Rate (\%)} = \frac{Q (100 - P)}{P} \times \frac{1}{R} \times 100 \quad (3)$$

Here, when the calculated dissolution rate exceeds 100%, the dissolution rate is assumed to be 100%.

Also, the temperature of the slurry is preferably from 30° to 80°C, more preferably from 40° to 70°C. The temperature of the slurry is preferably in the above range from the aspects of the dissolution of the water-soluble components (B, C) and the liquid conveyability thereof with a pump.

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A method for forming a slurry includes, for instance, a process comprising adding an entire amount or almost the entire amount of water to a mixing vessel at first, and in order or simultaneously adding the remaining components, preferably after a stage where a water temperature almost reaches an operable temperature. The usual order of addition comprises firstly adding liquid components such as a surfactant and a polyacrylate, and subsequently adding a water-soluble, powdery starting material such as soda ash. In addition, a small amount of the auxiliary components such as a dye is added. Finally, the water-insoluble component such as zeolite is added. In the addition of the water-insoluble component, for the purpose of improving blending efficiency, the water-insoluble component may be added in two or more separate portions. Also, the powdery starting materials may be previously blended, and the blended powder starting materials may then be added to an aqueous medium. Further, after the addition of the entire components, water may be added to adjust its viscosity or the water content of the slurry. After the addition of the entire components in the slurry, the components are blended for preferably 10 minutes or more, more preferably 30 minutes or more, to prepare a uniform slurry.

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5.2 Step (b) (Step for Preparation of Base Particles)

Step (b) comprises drying the slurry obtained in Step (a) to prepare base particles. As the drying method of the slurry, in order that the base particles have the localized structure of the components characteristic to the present invention, it is preferable that the slurry is instantaneously dried, and more preferably that spray-drying to form the resulting particles with a substantially spherical shape. The spray-drying tower may be either a countercurrent tower or concurrent tower, and the countercurrent tower is more preferable from the viewpoints of thermal efficiency and improvement in the particle mechanical strength of the resulting base particles. The finely powderizing device for the slurry may have any shapes of a pressure spray nozzle, a two-fluid spray nozzle, and a rotatable disc. From the viewpoint of having an average particle size of the resulting base particles of from 150 to 500 μm , preferably from 180 to 300 μm , the pressure spray nozzle is particularly preferable.

It is preferable that the temperature of the high-temperature gas supplied to the drying tower is usually from 150° to 300°C, preferably from 170° to 250°C. The temperature is desirably lower than the upper limit of the above range, so that organic compounds in the solid

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product adhered to the spray-drying tower is less likely to be combusted when continuous operation is carried out, which preventing troubles. In addition, it is preferable that the temperature of the gas exhausted from the drying tower is usually from 70° to 125°C, preferably from 80° to 115°C. The temperature of the exhausted gas is desirably lower than the upper limit of the above range, from the viewpoint of imparting good thermal efficiency of the drying tower.

10

5.3 Step (c) (Step of Adding Surfactant)

Step (c) comprises adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby. The surfactant can be supported by the base particles by using known mixers in a batch process or continuous process. Also, in a case where the method of the present invention is carried out in a batch process, the method for supplying the base particles and the surfactant can be carried out, for instance, by the following various embodiments. Incidentally, each of the

15

20

25

(1) Embodiment comprising supplying base particles in the mixer in advance; and then adding a surfactant thereto.

(2) Embodiment comprising simultaneously supplying each

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of base particles and a surfactant in the mixer in small amounts at a time.

(3) Embodiment comprising supplying a part of base particles in the mixer in advance; and supplying the
5 remaining base particles and a surfactant thereto in small amounts at a time.

Among these embodiments, (1) is particularly preferable. Also, the surfactant is preferably added in a liquid state, and it is more preferable that the
10 surfactant in a liquid state is supplied by spraying.

Of the surfactants which are present in the form of solids or pastes when heated to a temperature within a practical temperature range, those surfactants can be added to the base particles in the form of a liquid
15 mixture or aqueous solution by dispersing or dissolving the solid or paste-like surfactant in a low-viscosity surfactant, such as a nonionic surfactant, an aqueous solution of a nonionic surfactant or water, to prepare a liquid mixture or aqueous solution of surfactants. By
20 this method, the surfactants which are present in the form of solids or pastes can be easily added to the base particles, thereby making it further advantageous in the production of the uni-core detergent particles. The mixing ratio of the low-viscosity surfactant or water to
25 the solid or paste-like surfactant is preferably such that

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the resulting liquid mixture or aqueous solution has a viscosity in a sprayable range. For instance, as to the case of mixing a polyoxyethylene dodecyl ether and sodium dodecylbenzenesulfonate, the liquid mixture of surfactants which is easily sprayable can be obtained by adjusting its mixing ratio to 1:1.4 or less.

Examples of the method for preparing the above liquid mixture include a method of supplying a solid or paste-like surfactant to a low-viscosity surfactant or water; or a method of neutralizing an acid precursor of a surfactant in a low-viscosity surfactant or water with an alkalizing agent, for instance, an aqueous sodium hydroxide or an aqueous potassium hydroxide, to prepare a liquid mixture of surfactants.

In addition, in Step (c), an acid precursor of an anionic surfactant can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the acid precursor of an anionic surfactant, there can be achieved high concentration of the surfactants, control for an oil-absorbing ability of the base particles, and improvements in properties and quality, such as prevention of exudation of the nonionic surfactant and the flowability, of the resulting detergent particles.

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Examples of the acid precursor of an anionic surfactant which can be used in the present invention include alkylbenzenesulfonic acids, alkylether or alkenylether sulfuric acids, alkylsulfuric or
5 alkenylsulfuric acids, α -olefinsulfonic acids, α -sulfonated fatty acids, alkylether or alkenylether carboxylic acids, fatty acids, and the like. The fatty acid preferably is added after adding the surfactant.

The amount of the acid precursor of an anionic
10 surfactant used is preferably from 0.5 to 30 parts by weight, more preferably from 1 to 20 parts, based on 100 parts by weight of the base particles. When the amount of the acid precursor of an anionic surfactant used is in the above range, the uni-core properties of the detergent
15 particles can be maintained, so that the detergent particles can show good high-speed dissolution. As the method for adding the acid precursor of an anionic surfactant, it is preferable that those of a liquid state at an ambient temperature are supplied by spraying, and
20 that those of a solid state at an ambient temperature can be added as a powder, or they may be supplied by spraying after melting the solid. Here, in a case of adding as a powder, it is preferable that the temperature of the detergent particles in the mixer is raised to a point
25 where the powder melts.

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Conventional mixers can be used as devices preferably usable for Step (c), for instance, Henschel Mixer (manufactured by Mitsui Miike Machinery Co., Ltd.); High-Speed Mixer (Fukae Powtec Corp.); Vertical Granulator
5 (manufactured by Powrex Corp.); Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.); PLOUGH SHARE Mixer (manufactured by PACIFIC MACHINERY & ENGINEERING Co., LTD.); V-type Mixer (manufactured by Fuji Paudal Co., Ltd.); Ribbon Mixer (manufactured by Fuji Paudal Co.,
10 Ltd.); Nauta Mixer (manufactured by Hosokawa Micron Corp.); and SV Mixer (Shinko Panteck Co., Ltd.).

From the viewpoint of producing the uni-core particles, those devices less likely to have strong shearing force against the base particles; i.e. those
15 mixers less likely to cause breakdown of the base particles, are preferable mixers, and from the viewpoint of dispersion efficiency of the surfactants, those devices with good mixing efficiency are also preferable. A particular preference is given to a mixer containing an
20 agitating shaft arranged along the center line of a horizontal, cylindrical blending vessel and agitating impellers arranged on the agitating shaft, to carry out blending of the powders, including Lödige Mixer, and PLOUGH SHARE Mixer.

25 In addition, those mixers listed above in a

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continuous process can be also used to support the surfactant by the base particles. Also, as the mixers for a continuous process other than those listed above, there can be used, for instance, Flexo Mix (manufactured by
5 Powrex Corp.); Flow Jet Mixer (manufactured by Funken Powtechs, Inc.); Spiral Pin Mixer (manufactured by PACIFIC MACHINERY & ENGINEERING Co., LTD.); "TURBULIZER" (manufactured by Hosokawa Micron Corp.), and the like.

In addition, in Step (c), a melting point-elevating
10 agent of the nonionic surfactant, which is a water-soluble nonionic organic compound (hereinafter referred to as "melting point-elevating agent") having a melting point of from 45° to 100°C and a molecular weight of from 1,000 to 30,000, and an aqueous solution of the melting
15 point-elevating agent can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, after adding a surfactant, or previously mixing with a surfactant. By adding the melting point-elevating agent, the caking
20 properties and the exudation property of the surfactants in the detergent particles can be suppressed. Examples of the melting point-elevating agent which can be used in the present invention include polyethylene glycols, polypropylene glycols, polyoxyethylene alkyl ethers,
25 pluronic nonionic surfactants, and the like.

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The amount of the melting point-elevating agent used is preferably from 0.5 to 5 parts by weight, more preferably from 0.5 to 3 parts by weight, based on 100 parts by weight of the base particles. The amount is
5 preferably in the above range from the aspects of maintaining the uni-core property of the detergent particles, having high-speed dissolution, and suppressing the exudation property and the caking properties. As a method for adding the melting point-elevating agent, a
10 method comprising previously mixing a melting point-elevating agent with a surfactant, or a method comprising adding a melting point-elevating agent after adding a surfactant is highly advantageous in suppressing the exudation property and the caking properties of the
15 resulting detergent particles.

As to the temperature within the mixer used in Step (c), it is more preferable that mixing is carried out by heating to a temperature equal to or higher than the melting point of the surfactant. Here, the temperature to
20 be heated is preferably a temperature equal to or higher than the melting point of the surfactant added in order to promote the support of the surfactant, and the practical temperature range is preferably a temperature higher than the melting point by 0° to 50°C, more preferably by 10° to
25 30°C. In addition, in a case where an acid precursor of

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the anionic surfactant is added in Step (c), it is more preferable to mix the components after heating to a temperature at which the acid precursor of the anionic surfactant can react.

5 In Step (c), the mixing time in a batch process and the average retention time in the mixing in a continuous process for obtaining the desired detergent particles are not limited to specified ones, and are preferably from 1 to 20 minutes, more preferably from 2 to 10 minutes.

10 In addition, in a case where an aqueous solution of a surfactant or an aqueous solution of a melting point-elevating agent is added, a step of drying excess water contents during mixing and/or after mixing may be included.

15 In addition, in Step (c), a powdery surfactant and/or a powdery builder for detergents can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the powdery builder for
20 detergents, the particle size of the detergent particles can be controlled, and an improvement in detergency can be achieved. Particularly in a case where an acid precursor of the anionic surfactant is added, it is more effective to add a powdery builder showing alkaline property prior
25 to adding the acid precursor from the viewpoint of

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accelerating the neutralization reaction. Incidentally, the term "powdery builder" mentioned herein refers to an agent for enhancing detergency other than surfactants which is in a powdery form. Concrete examples thereof

5 include base materials showing metal ion capturing ability, such as zeolite and citrates; agents showing alkalizing ability, such as sodium carbonate and potassium carbonate; base materials showing both metal ion capturing agent and alkalizing ability, such as crystalline

10 silicates; and base materials enhancing ionic strength, such as sodium sulfate.

In addition, crystalline silicates disclosed in Japanese Patent Laid-Open No. 5-279013, column 3, line 17 to column 6, line 24 (in particular, a method comprising

15 baking at a temperature of 500° to 1000°C, and crystallizing the baked mixture is preferable); Japanese Patent Laid-Open No. 7-89712, column 2, line 45 to column 9, line 34; and Japanese Patent Laid-Open No. 60-227895, page 2, lower right column, line 18 to page 4, upper right

20 column, line 3 (particularly the silicates in Table 2 are preferable) have been recently remarked as detergent starting materials and can be used as powdery builders. This is because these base materials have both the alkalizing ability and the metal ion capturing ability.

25 Here, the alkali metal silicates having an $\text{SiO}_2/\text{M}_2\text{O}$ ratio,

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wherein M is an alkali metal, of from 0.5 to 3.2, preferably from 1.5 to 2.6, can be favorably used. A preferable blending method so as not to impair the performance of the base material and the quality of the detergent includes a method comprising finely pulverizing a crystalline silicate to a size of from 1 to 20 μm or so, preferably from 1 to 10 μm or so, and then using the resulting finely pulverized product as a surface modifying agent. Here, as a surface modifying agent, the finely pulverized product can be used as an admixture with other fine powders such as crystalline and/or amorphous aluminosilicates and inorganic salts such as sodium sulfate. Here, for the purpose of preventing deterioration of particles caused by the aggregation of crystalline silicates owing to the absorption of moisture or carbon dioxide, it is preferable to mix these fine powders.

The amount of the powdery builder for detergents used is preferably from 0.5 to 12 parts by weight, more preferably from 1 to 6 parts by weight, based on 100 parts by weight of the base particles. When the amount of the powdery builder for detergents used is in the above range, the uni-core property of the detergent particles can be maintained, good high-speed dissolution can be obtained, and the particle size can be favorably controlled.

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5.4 Surface-Modifying Step

In the present invention, in order to surface-modify the uni-core detergent particles in which the surfactant is supported by the base particle in Step (c), a surface-modifying step comprising adding various surface coating agents described below, such as (1) a fine powder, (2) a water-soluble polymer, or (3) a fatty acid. The surface-modifying step may be carried out in one step, or it may be repeated in two steps.

When the surface of the uni-core detergent particles of the present invention is coated, since the flowability and the non-caking properties of the detergent particles are likely to be improved, it is preferable to include the surface-modifying step. The devices used in the surface-modifying step are not limited to specified ones, and any of known mixers can be used. It is preferable to use the mixers exemplified in Step (c) above. Each of the surface coating agents will be explained below.

(1) Fine Powder

It is preferable that the average particle size of the primary particles is 10 μm or less, preferably from 0.1 to 10 μm . When the average particle size is in this range, it is favorable from the viewpoints of improvements in the coating ratio of the surfaces of the uni-core detergent particles, so that the flowability and the

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anti-caking property of the detergent particles are improved. The average particle size of the fine powder can be measured by a method utilizing light scattering, for instance, by a particle analyzer (manufactured by
5 Horiba, LTD.), or it may be measured by a microscopic observation. In addition, it is preferable that the fine powder has a high ionic exchange capacity or a high alkalizing ability from the aspect of detergency.

The fine powder is desirably aluminosilicates, which
10 may be crystalline or amorphous. Besides the aluminosilicates, inorganic fine powders, such as calcium silicate, silicon dioxide, bentonite, talc, clay, amorphous silica derivatives, silicate compounds such as crystalline silicate compounds, and the like are
15 preferable. In addition, a metal soap and a powdery surfactant such as alkylsulfates of which primary particles have a size of 10 μm or less, preferably 0.1 to 10 μm can be similarly employed.

The amount of the fine powder used is preferably from
20 0.5 to 40 parts by weight, more preferably from 1 to 30 parts by weight, still more preferably from 2 to 20 parts by weight, based on 100 parts by weight of the uni-core detergent particles. When the amount of the fine powder is in the above range, the flowability is improved,
25 thereby giving a good texture to consumers.

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(2) Water-Soluble Polymer

Examples of the water-soluble polymer include carboxymethyl cellulose, polyethylene glycols, and polycarboxylates such as sodium polyacrylates and acrylic acid-maleic acid copolymers and salts thereof. The amount of the water-soluble polymer used is preferably from 0.5 to 10 parts by weight, more preferably from 1 to 8 parts by weight, still more preferably from 2 to 6 parts by weight, based on 100 parts by weight of the uni-core detergent particles. When the amount of the water-soluble polymer is in the above range, a powder showing good flowability and anti-caking properties can be obtained while the detergent particles can maintain their uni-core property and have good high-speed dissolution.

As a method for adding the water-soluble polymer, those in a liquid state at an ambient temperature are preferably supplied by spraying.

(3) Fatty Acid

Examples of the fatty acid include fatty acids having 10 to 22 carbon atoms. The amount of the fatty acid used is preferably from 0.5 to 5 parts by weight, more preferably from 0.5 to 3 parts by weight, based on 100 parts by weight of the uni-core detergent particles. In a case of those in a solid state at an ambient temperature, it is preferable that they are heated to a temperature

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showing flowability, and then supplied by spraying.

6. Composition of Multi-Core Detergent Particles and
Production Method Thereof

5 The multi-core detergent particles of the present
invention may be those in which the above base particles
constituting the uni-core detergent particles are
aggregated, or those in which sodium carbonate, and the
like used as a core are aggregated, as long as they are
10 capable of generating given bubbles. In particular, by
using the base particles constituting the uni-core
detergent particles, the localized property of the base
particles causes to enhance the dissolution property, and
the high-speed dissolution can be further improved.
15 Therefore, as the base particles used herein, the base
particles in the uni-core detergent particles can be used,
and as the surfactant which can be supported by the base
particles, the surfactant mentioned for the uni-core
detergent particles can be used. In addition, the
20 multi-core detergent particles can be easily formed by
increasing the amount of the surfactant. Incidentally,
the dissolution acceleration between the base particles
can be enhanced by using a foaming agent such as sodium
bicarbonate or a percarbonate.

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7. Properties of the Multi-Core Detergent Particles

The multi-core detergent particles of the present invention have high-speed dissolution. The term "high-speed dissolution of the detergent particles" as
5 defined in the present invention has the same definition as that of the high-speed dissolution of the uni-core detergent particles. In addition, the detergent particles of the present invention show similarly high dissolution rate to the uni-core detergent particles, thereby showing
10 an extremely high high-speed dissolution property notably distinguishable from the dissolution property of conventional detergents. In the present invention, as long as either the 60-seconds dissolution rate or the 30-seconds dissolution rate of the detergent particles
15 satisfies within a given range, such detergent particles reveal excellent high-speed dissolution property, and it is more preferable that both the dissolution rates satisfy within a given range.

As to the bulk density, the average particle size,
20 the flowability, the caking property, and the exudation property, it is preferable that the multi-core detergent particles have similar properties to those for the uni-core detergent particles described in Sections 4.2.3 through 4.2.7 above.

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8. Detergent Composition

The detergent composition of the present invention includes the uni-core detergent particles of the present invention or the multi-core detergent particles of the present invention in an amount of 50% by weight or more, preferably 80% by weight or more in the detergent composition, thereby making it possible to provide a detergent composition having high-speed dissolution.

In the above detergent composition, in the process of dissolving the detergent composition in water, the number of particles in the particles constituting the detergent composition which release bubbles from the inner portion of the particles of the size of one-tenth or more the particle size of the particles constituting the detergent composition occupies 50% or more, preferably 80% or more, of the entire number of particles in the particles constituting the detergent composition.

The detergent composition of the present invention may include components other than the uni-core detergent particles of the present invention or the multi-core detergent particles of the present invention. As these components, there can be included components generally used for known detergent compositions.

25 Preparation of Base Particles

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Base Particles 1 were prepared by the following procedures.

To a 1 m³-mixing vessel having agitation impellers was added 465 kg of water. After the water temperature
5 reached 55°C, 48 kg of a 50% by weight-aqueous sodium dodecylbenzenesulfonate solution and 135 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. After stirring the mixture for 15 minutes, 120 kg of sodium carbonate, 60 kg of sodium sulfate, 9 kg of
10 sodium sulfite, and 3 kg of a dye were added. After stirring the resulting mixture for additional 15 minutes, 300 kg of zeolite was added thereto, and the obtained mixture was stirred for 30 minutes to give a uniform slurry. The final temperature of this slurry was 58°C.
15 In addition, the water content in this slurry was 50% by weight, and the dissolution rate of the aqueous components including sodium polyacrylate, sodium carbonate, sodium sulfate, and sodium sulfite was 100%.

This slurry was sprayed with a pressure spray nozzle
20 arranged near the top of a spray-drying tower at a spraying pressure of 25 kg/cm². A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 225°C and exhausted from the top of the tower at a temperature of
25 105°C. The composition of the resulting Base Particles 1

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and the properties thereof are shown in Tables 1 and 2.
Also, an example of an SEM image of a split cross section
when measuring the particle size and the pore size of an
inner portion of the particles for Base Particles 1 is
5 shown in Figure 8. Incidentally, with regard to Base
Particles 1, it was confirmed that pores with a pore size
of from 1/10 to 4/5 the particle size were found in 88% of
the particles. Here, an average value for pore
size/particle size in 88% of the particles was 3.1/5.

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Table 1

5	Components		% by weight
	Component A	Zeolite ^{*1)}	50

10	Component B	Sodium Polyacrylate ^{*2)}	9

	Component C	Sodium Carbonate ^{*3)}	20
		Sodium Sulfate	10
		Sodium Sulfite	1.5
15	-----		
	Others	Sodium Dodecylbenzene-sulfonate ^{*4)}	4
		Dye ^{*5)}	0.5
		Water	5
20	-----		

Remarks *1): Zeolite 4A-type, average particle size: 3.5 μ m (manufactured by Tosoh Corporation).

25 *2): Average molecular weight: 10000.

*3): "DENSE ASH" (manufactured by Central Glass Co., Ltd.).

*4): "NEOPELEX F-65" (manufactured by Kao Corporation).

30 *5): Fluorescent dye "CINOPEARL CBS-X" (manufactured by Ciba-Geigy).

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Table 2

5	Properties	
	Bulk Density	620 g/liter
	Average Particle Size	225 μm
	Particle Mechanical Strength	250 kg/cm^2
	Oil-Absorbing Ability	52 ml/100 g
	Water Content	5% by weight
10		

Base Particles 2 to 4 were prepared in the same manner as above. The composition and the properties of each of Base Particles are shown in Table 3. Also, examples of SEM images of a split cross section when measuring the particle size and the pore size of an inner portion of the particles for each of Base Particles 2 to 4 are shown in Figures 9 to 11. With regard to Base Particles 2, it was confirmed that pores with a pore size of from 1/10 to 4/5 the particle size were found in 85% of the particles. Here, an average value for pore size/particle size in 85% of the particles was 2.2/5. With regard to Base Particles 3, it was confirmed that pores with a pore size of from 1/10 to 4/5 the particle size were found in 91% of the particles. Here, an average value for pore size/particle size in 91% of the particles was 1.3/5. With regard to Base Particles 4, it was confirmed that pores with a pore size of from 1/10 to 4/5

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the particle size were found in 72% of the particles.
Here, an average value for pore size/particle size in 72%
of the particles was 3.4/5.

Table 3

	Base Particles 2	Base Particles 3	Base Particles 4
<u>Composition of Base Particles (% by weight)</u>			
<u>Component A</u>			
Zeolite	50	67	40
<u>Component B</u>			
Sodium Polyacrylate	9	9	15
<u>Component C</u>			
Sodium Carbonate	20	17	28
Sodium Sulfate	10		10
Sodium Sulfite	1	1	1
<u>Others</u>			
Sodium Dodecylbenzensulfonate	4		
Auxiliary Components (Dyes, etc.)	1	1	1
Water	5	5	5
<u>Slurry Formations (% by weight)</u>			
Water Content of Aqueous Slurry	42	38	54
Dissolution Rate of Water-Soluble Components	90	100	100
<u>Spray Drying</u>			
Gas Supplying Temp. (°C)	227	234	228
Gas Exhaustion Temp. (°C)	106	109	108
Spraying Pressure (kg/cm ²)	25	25	25
<u>Properties of Base Particles</u>			
Bulk Density (g/liter)	640	720	610
Average Particle Size (μ m)	235	250	215
Particle Mechanical Strength (kg/cm ²)	320	370	230
Oil-Absorbing Ability (ml/100g)	48	44	65
Water Content (% by weight)	3.2	3.4	3.0

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Also, these base particles were analyzed by FT-IR/PAS, SEM observation, and EDS. As a result, it was confirmed that the base particles had a coating-type particle structure wherein the proportion of the zeolite was high in the inner portion of the particles, and the aqueous polymer and the aqueous salts were largely present near the surface of the particles.

Example 1

10 The detergent particles of the present invention were obtained by adding a surfactant to Base Particles 1 in a proportion shown in Table 4 so as to support the surfactant by Base Particles 1. Twenty-three parts by weight of a nonionic surfactant shown in Table 4 were
15 heated to a temperature of 50°C. Next, 100 parts by weight of Base Particles were supplied in Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.; capacity: 20 liters; equipped with a jacket), and agitation was initiated with the mixer having a main axis (150 rpm) and
20 a chopper (4,000 rpm). Incidentally, heated water of 60°C was supplied in the jacket at a flow rate of 10 liters/minute. To the above mixer, the nonionic surfactant was added in a period of 2 minutes, and thereafter the added mixture was agitated for 4 minutes,
25 and the resulting mixture was discharged.

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The properties of the resulting detergent particles are shown in Table 4.

The hollowness of the detergent particles was measured. As a result, it was found that pores with a pore size of 1/10 to 4/5 the particle size were found in 86% of the particles.

Further, the dissolution behavior of the detergent particles of Example 1 was observed by a digital microscope. As a result, it was confirmed that bubbles with a size of 1/10 or more of the particle size were released from 87% of the particles. Here, an average value for size of released bubbles/particle size in 87% of the particles was 3.0/5. Further, the surface of the detergent particles was surface-coated with 10 parts by weight of a crystalline aluminosilicate. The properties of the resulting detergent particles showed improvements in quality such as flowability with maintaining their dissolution property.

Example 2

The detergent particles of the present invention were obtained by adding to Base Particles 1, a nonionic surfactant solution previously mixed with a polyethylene glycol shown in Table 4.

Twenty-one parts by weight of a nonionic surfactant

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and 2 parts by weight of a polyethylene glycol each shown in Table 4 were heated to a temperature of 70°C, to prepare a liquid mixture. Next, 100 parts by weight of Base Particles were supplied in the same Lödige Mixer as in Example 1, and agitation was initiated with the mixer having a main axis (150 rpm) and a chopper (4,000 rpm). Incidentally, heated water of 75°C was supplied in the jacket at a flow rate of 10 liters/minute. To the above mixer, the liquid mixture was added in a period of 2 minutes, and thereafter the added mixture was agitated for 4 minutes. Further, the surface of the detergent particles was surface-coated with 10 parts by weight of a crystalline aluminosilicate.

The properties of the resulting detergent particles are shown in Table 4.

The hollowness of the detergent particles was measured. As a result, it was found that pores with a pore size of 1/10 to 4/5 the particle size were found in 87% of the particles. An example of an SEM image of a split cross section when measuring the particle size and the pore size of an inner portion of the particles for the detergent particles is shown in Figure 12.

Further, the dissolution behavior of the detergent particles was observed in the same manner as in Example 1. As a result, it was confirmed that bubbles with a size of

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1/10 or more of the particle size were released from 89% of the particles. Here, an average value for size of released bubbles/particle size in 89% of the particles was 2.8/5. In addition, by including the polyethylene glycol, the anti-caking properties of the detergent particles can be further improved, and the exudation of the nonionic surfactant can be further suppressed.

Example 3

10 The detergent particles of the present invention were obtained by adding to Base Particles 1, surfactants and other components in proportions shown in Table 4.

Fifteen parts by weight of a nonionic surfactant, 15 parts by weight of an anionic surfactant, and 1 part by weight of a polyethylene glycol each shown in Table 4 were heated to a temperature of 70°C, to prepare a liquid mixture. Next, the detergent particles were produced in the same manner as in Example 2 except that the liquid mixture was added to the mixer in a period of 3 minutes, and thereafter the added mixture was agitated for 5 minutes.

The properties of the resulting detergent particles are shown in Table 4.

The hollowness of the detergent particles was measured. As a result, it was found that pores with a

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pore size of $1/10$ to $4/5$ the particle size were found in 90% of the particles.

Further, the dissolution behavior of the detergent particles was observed in the same manner as in Example 1.

5 As a result, it was confirmed that bubbles with a size of $1/10$ or more of the particle size were released from 88% of the particles. Here, an average value for size of released bubbles/particle size in 88% of the particles was $2.7/5$.

10

Example 4

As a method of adding an anionic surfactant, an acid precursor of an anionic surfactant was used in such a manner that a nonionic surfactant was supplied into a
15 mixer without mixing with the acid precursor, and thereafter an acid precursor of an anionic surfactant, dodecylbenzenesulfonic acid, was supplied into the mixer to obtain the detergent particles of the present invention. As the base particles, Base Particles 1 were
20 used.

Fifteen parts by weight of a nonionic surfactant and 1 part by weight of a polyethylene glycol shown in Table 4 were heated to a temperature of 70°C , to prepare a liquid mixture. Next, 100 parts by weight of Base Particles were
25 supplied in the same Lödige Mixer as in Example 1, and

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agitation was initiated with the mixer having a main axis (150 rpm) and a chopper (4,000 rpm). Incidentally, heated water of 75°C was supplied in the jacket at a flow rate of 10 liters/minute. To the above mixer, the liquid mixture
5 was added in a period of 2 minutes, and thereafter the added mixture was agitated for 3 minutes. Next, 15 parts by weight of an acid precursor of an anionic surfactant heated to 45°C were supplied in a period of 2 minutes, and thereafter the added mixture was agitated for 4 minutes.
10 Further, the surface of the detergent particles was surface-coated with 5 parts by weight of a crystalline aluminosilicate.

The properties of the resulting detergent particles are shown in Table 4.

15 The hollowness of the detergent particles was measured. As a result, it was found that pores with a pore size of 1/10 to 4/5 the particle size were found in 85% of the particles.

Further, the dissolution behavior of the detergent
20 particles was observed in the same manner as in Example 1. As a result, it was confirmed that bubbles with a size of 1/10 or more of the particle size were released from 86% of the particles. Here, an average value for size of released bubbles/particle size in 86% of the particles was
25 2.8/5.

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Example 5

The detergent particles of the present invention were obtained by adding to Base Particles 1, surfactants and other components in proportions shown in Table 4.

5 Twenty parts by weight of a nonionic surfactant shown in Table 4 were heated to a temperature of 50°C. Next, 100 parts by weight of Base Particles were supplied in the same Lödige Mixer as in Example 1, and agitation was initiated with the mixer having a main axis (150 rpm) and
10 a chopper (4,000 rpm). Incidentally, heated water of 75°C was supplied in the jacket at a flow rate of 10 liters/minute. To the above mixer, the nonionic surfactant was added in a period of 2 minutes, and thereafter the added mixture was agitated for 4 minutes.
15 Next, 3 parts by weight of an alkaline builder shown in Table 4 were supplied therein, and the mixture was agitated for one minute. Thereafter, a molten product of an acid precursor of an anionic surfactant shown in Table 4 at 80°C was supplied thereinto, and the mixture was
20 agitated for 2 minutes, and the resulting mixture was discharged. Further, the surface of the detergent particles was surface-coated with 8 parts by weight of a crystalline aluminosilicate.

25 The properties of the resulting detergent particles are shown in Table 4.

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The hollowness of the detergent particles was measured. As a result, it was found that pores with a pore size of $1/10$ to $4/5$ the particle size were found in 86% of the particles.

5 Further, the dissolution behavior of the detergent particles was observed in the same manner as in Example 1. As a result, it was confirmed that bubbles with a size of $1/10$ or more of the particle size were released from 88% of the particles. Here, an average value for size of
10 released bubbles/particle size in 88% of the particles was $2.9/5$.

Example 6

The detergent particles were obtained in the same
15 manner as in Example 3 except for sieving Base Particles 1 and obtaining as Base Particles particles classified between $125\text{ }\mu\text{m}$ -sieve opening and $180\text{ }\mu\text{m}$ -sieve opening.

The properties of the resulting detergent particles are shown in Table 4.

20 The split cross section of the detergent particles was observed by SEM. As a result, it was confirmed that the detergent particles had a particle structure of the multi-core detergent particles. Moreover, the dissolution behavior of the detergent particles was observed in the
25 same manner as in Example 1. As a result, it was

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confirmed that bubbles with a size of 1/10 or more of the particle size were released from 68% of the particles. Here, an average value for size of released bubbles/particle size in 68% of the particles was 1.5/10.

Table 4

[illegible]

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Remarks of Table 4:

- 5 *1: "EMULGEN 108KM" (manufactured by Kao Corporation), average additional molar number of ethylene oxide: 8.5.
- *2: "NEOPELEX F65," sodium dodecylbenzenesulfonate (manufactured by Kao Corporation).
- *3: "NEOPELEX FS," dodecylbenzenesulfonic acid (manufactured by Kao Corporation).
- *4: "LUNAC P-95" (manufactured by Kao Corporation).
- 10 *5: "K-PEG6000" (manufactured by Kao Corporation), average molecular weight: 8500.
- *6: Zeolite 4A-type (manufactured by Tosoh Corporation), average particle size: 3.5 μm .
- *7: Product prepared from Preparation Example 2 of Japanese Patent Laid-Open No. 9-132794, average particle size: 8 μm .
- 15 *8: Particles obtained by classifying and collecting particles sandwiched between a 125 μm -sieve opening and a 180 μm -sieve opening.
- 20

All amounts are expressed in parts by weight.

INDUSTRIAL APPLICABILITY

25 According to the present invention, there can be provided detergent particles having high-speed dissolution

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property. By the present invention, there can be achieved not only an effect of improving detergency by eluting the detergent components more quickly, but also a remarkable effect in detergent quality, in which substantially no
5 remaining insolubles of detergents are produced even when washing under a low mechanical power or a short period of time such as hand-washing cycle, gentle stirring cycle, and speed cycle generally employed in fully automatic washing machines today.

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CLAIMS

1. Detergent particles having an average particle size of from 150 to 500 μm , wherein the detergent
5 particles have a bulk density of 500 g/liter or more,
wherein the detergent particles have pores capable of releasing bubbles from an inner portion of the detergent particles in a process of dissolving the detergent particles in water, the bubbles having a size of one-tenth
10 or more of a particle size of the detergent particles, and
wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions that 1 g of the
15 detergent particles is supplied to a one-liter beaker having an inner diameter of 105 mm and charged with one-liter of hard water having 71.2 mg CaCO_3 /liter, wherein a molar ratio of Ca/Mg is 7/3, and stirred with a stirring rod of 35 mm in length and 8 mm in diameter at a
20 rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 μm as defined by JIS Z 8801, wherein the dissolution rate is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \quad (1)$$

25 wherein S is a weight (g) of the detergent particles supplied; and T is a dry weight (g) of remaining insolubles of the detergent particles remaining on the sieve when a liquid prepared under the above stirring

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conditions is filtered with the sieve, wherein drying conditions for the remaining insolubles are keeping at a temperature of 105°C for 1 hour, and then in a desiccator containing a silica gel therein at 25°C for 30 minutes.

5

2. Detergent particles having an average particle size of from 150 to 500 μm , wherein the detergent particles have a bulk density of 500 g/liter or more, wherein the detergent particles have pores capable of releasing bubbles from an inner portion of the detergent particles in a process of dissolving the detergent particles in water, the bubbles having a size of one-tenth or more of a particle size of the detergent particles, and wherein the detergent particles have a dissolution rate of 82% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 30 seconds under the stirring conditions that 1 g of the detergent particles is supplied to a one-liter beaker having an inner diameter of 105 mm and charged with one-liter of hard water having 71.2 mg CaCO_3 /liter, wherein a molar ratio of Ca/Mg is 7/3, and stirred with a stirring rod of 35 mm in length and 8 mm in diameter at a rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 μm as defined by JIS Z 8801, wherein the dissolution rate is calculated by Equation (1):

10

15

20

25

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \quad (1)$$

wherein S is a weight (g) of the detergent particles

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supplied; and T is a dry weight (g) of remaining insolubles of the detergent particles remaining on the sieve when a liquid prepared under the above stirring conditions is filtered with the sieve, wherein drying
5 conditions for the remaining insolubles are keeping at a temperature of 105°C for 1 hour, and then in a desiccator containing a silica gel therein at 25°C for 30 minutes.

3. The detergent particles according to claim 1 or
10 2, wherein each of the detergent particles comprises a base particle comprising a water-insoluble inorganic compound, a water-soluble polymer and a water-soluble salt, and a surfactant supported by the base particle, wherein the base particle has a localized structure in
15 which larger portions of the water-soluble polymer and the water-soluble salt are present near the surface of the base particle rather than in the inner portion thereof.

4. The detergent particles according to claim 3,
20 wherein the detergent particles comprise uni-core detergent particles.

5. The detergent particles according to claim 4,
wherein the uni-core detergent particles have pores in the
25 inner portion of classified uni-core detergent particles, the pores having a size of one-tenth to four-fifth a particle size of the uni-core detergent particles, wherein said classified uni-core detergent particles are obtained

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by determining an average particle size (median size)
based on weight of the uni-core detergent particles by the
use of a measuring device comprising sieves, a
sieve-opening of each sieve being from top to bottom
5 2000 μm , 1410 μm , 1000 μm , 710 μm , 500 μm , 355 μm , 250 μm ,
180 μm , and 125 μm , and a receiver, and taking out the
uni-core detergent particles classified between two sieves
sandwiching the average particle size.

10 6. The detergent particles according to claim 3,
wherein the base particles have pores in the inner portion
of classified based particles, the pores having a size of
one-tenth to four-fifth a particle size of the base
particles, wherein said classified base particles are
15 obtained by determining an average particle size (median
size) based on weight of the base particles by the use of
a measuring device comprising sieves, a sieve-opening of
each sieve being from top to bottom 2000 μm , 1410 μm ,
1000 μm , 710 μm , 500 μm , 355 μm , 250 μm , 180 μm , and
20 125 μm , and a receiver, and taking out the base particles
classified between two sieves sandwiching the average
particle size.

7. The detergent particles according to claim 3,
25 wherein the base particles comprise:
20 to 90% by weight of the water-insoluble inorganic
compound;
2 to 30% by weight of the water-soluble polymer; and

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5 to 78% by weight of the water-soluble salt.

8. The detergent particles according to claim 3,
wherein a surfactant is supported by the base particles in
5 an amount of 5 to 80 parts by weight, based on 100 parts
by weight of the base particles.

9. The detergent particles according to any one of
claims 6 to 8, wherein the detergent particles comprise
10 uni-core detergent particles.

10. Uni-core detergent particles, each of which
comprises a base particle comprising a water-insoluble
inorganic compound, a water-soluble polymer and a
15 water-soluble salt, and a surfactant supported by the base
particle, wherein the uni-core detergent particles have an
average particle size of from 150 to 500 μm , wherein the
uni-core detergent particles have a bulk density of
500 g/liter or more, wherein the base particle has a
20 localized structure in which larger portions of the
water-soluble polymer and the water-soluble salt are
present near the surface of the base particle rather than
in the inner portion thereof, and wherein the detergent
particles have a dissolution rate of 90% or more under
25 conditions as set forth in claim 1, or a dissolution rate
of 82% or more under conditions as set forth in claim 2.

11. A method for producing the detergent particles

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as defined in any one of claims 4 to 10, comprising the steps of:

- 5 Step (a): preparing a slurry containing a water-insoluble inorganic compound, a water-soluble polymer, and a water-soluble salt, wherein 60% by weight or more of water-soluble components including the water-soluble polymer and the water-soluble salt is dissolved in the slurry;
- 10 Step (b): spray-drying the slurry obtained in Step (a) to prepare base particles containing a water-insoluble inorganic compound, a water-soluble polymer, and a water-soluble salt; and
- 15 Step (c): adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby.

20 12. The method according to claim 11, further comprising a surface-modifying step.

13. A detergent composition comprising the detergent particles as defined in any one of claims 1 to 10 in an amount of 50% by weight or more.

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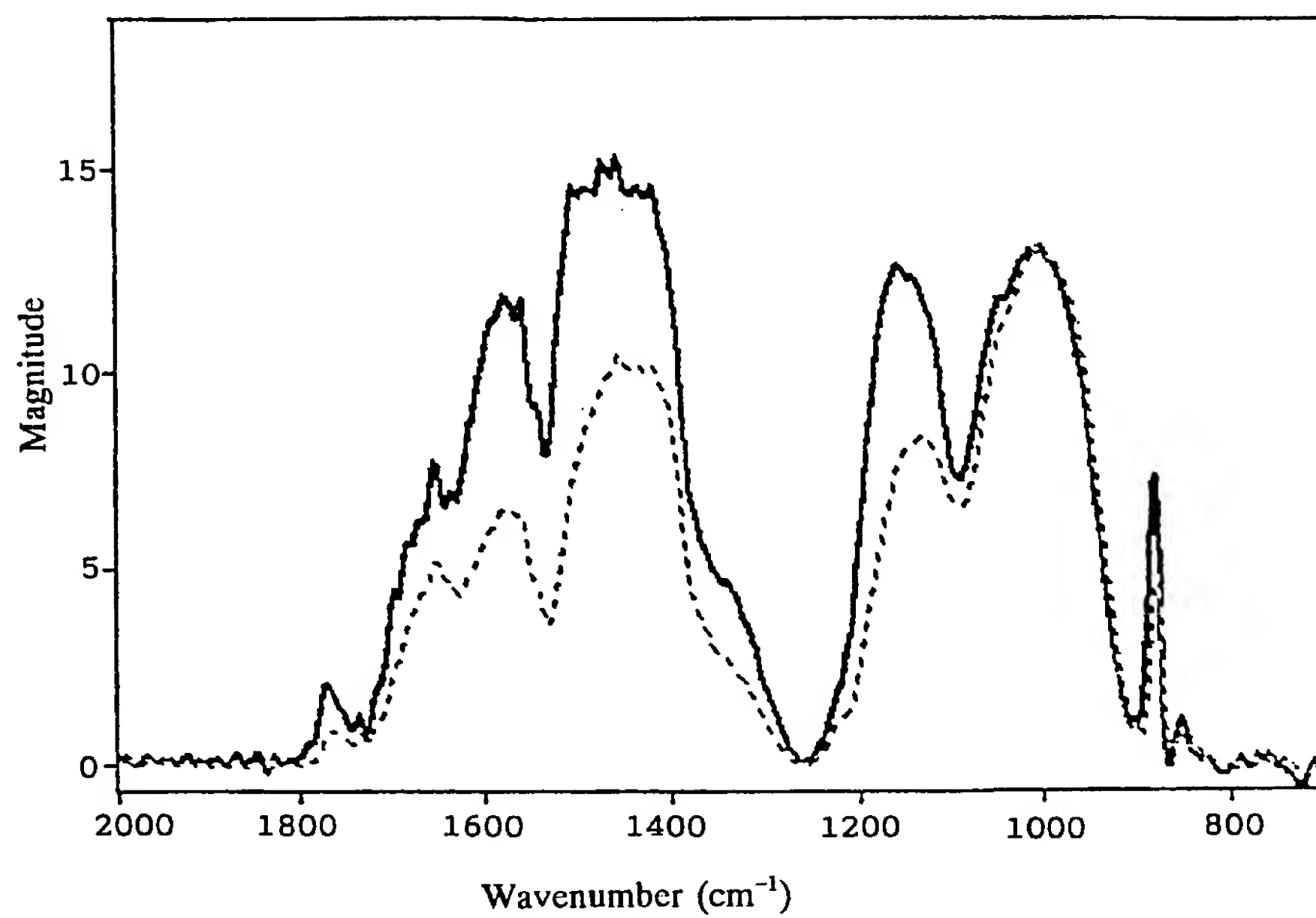


FIG. 1

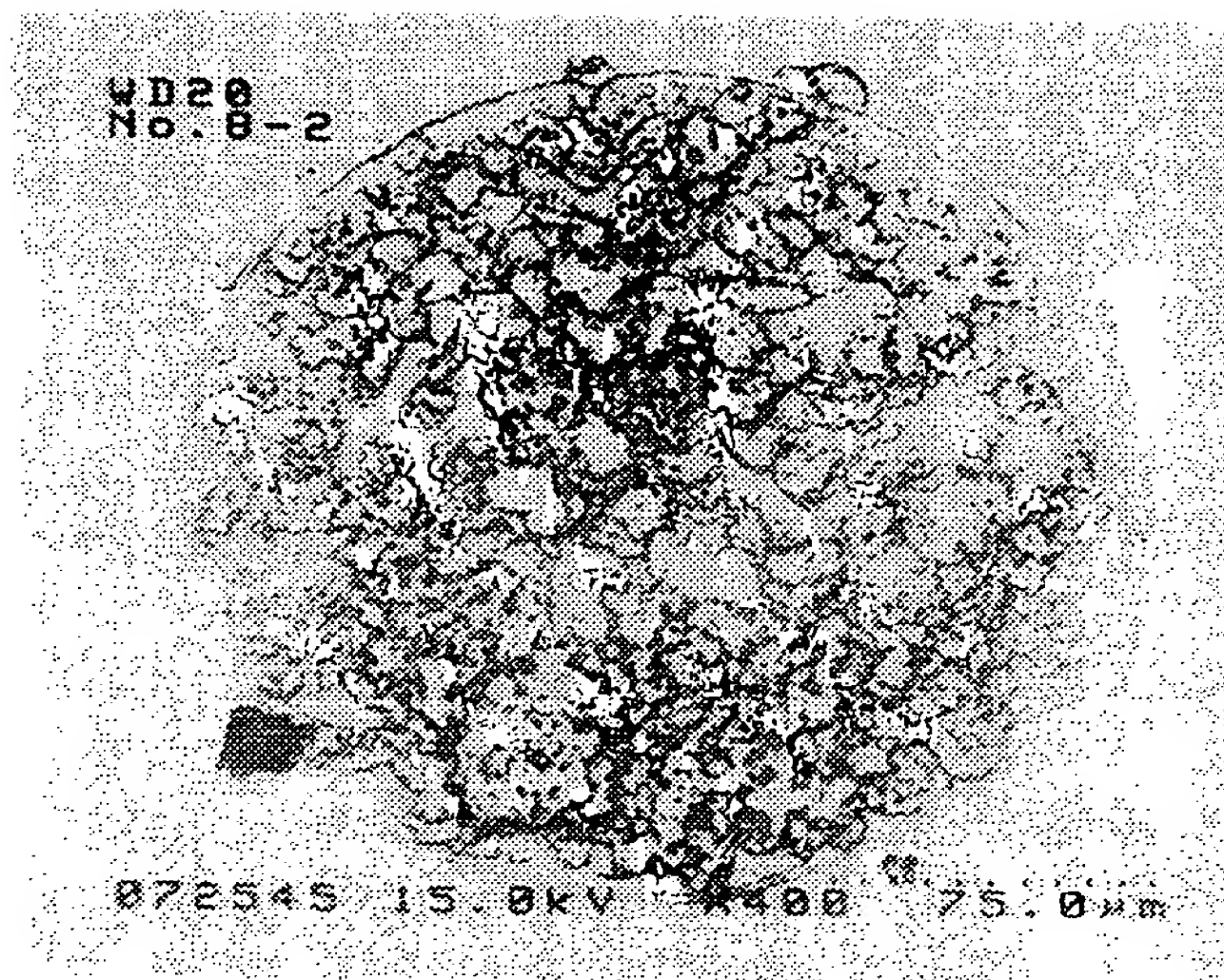


FIG. 2

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FIG. 3

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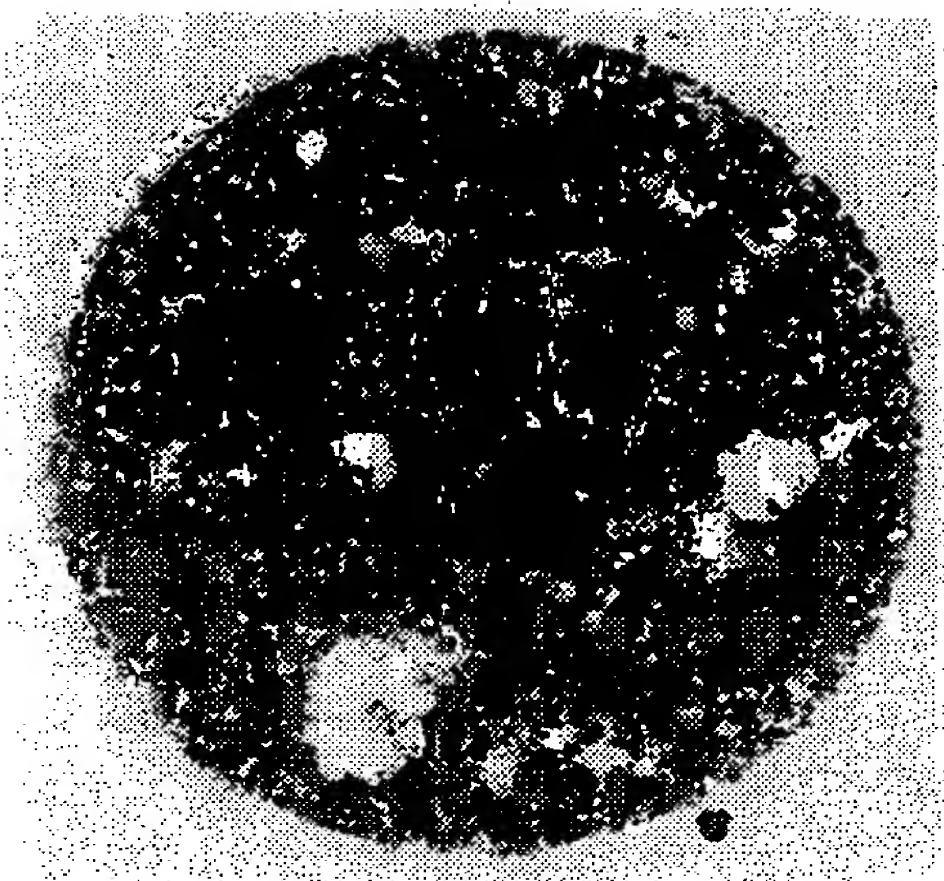


FIG. 4

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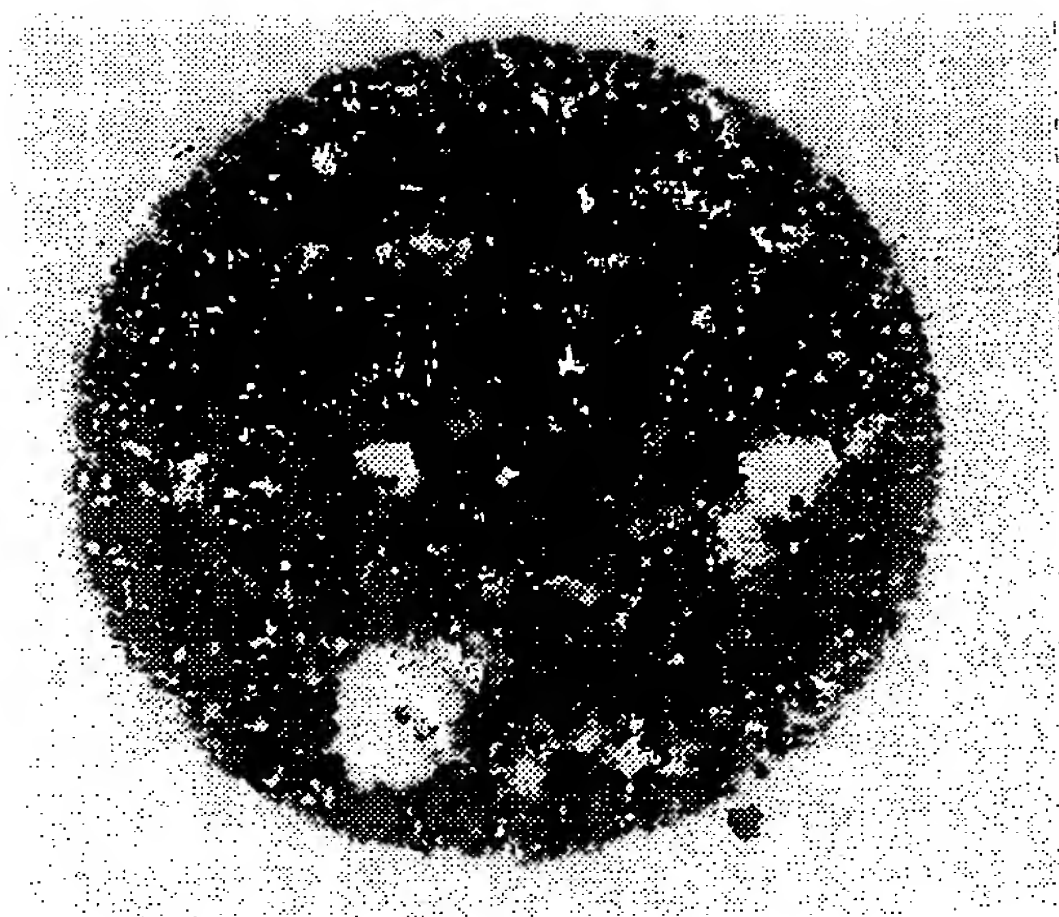


FIG. 5

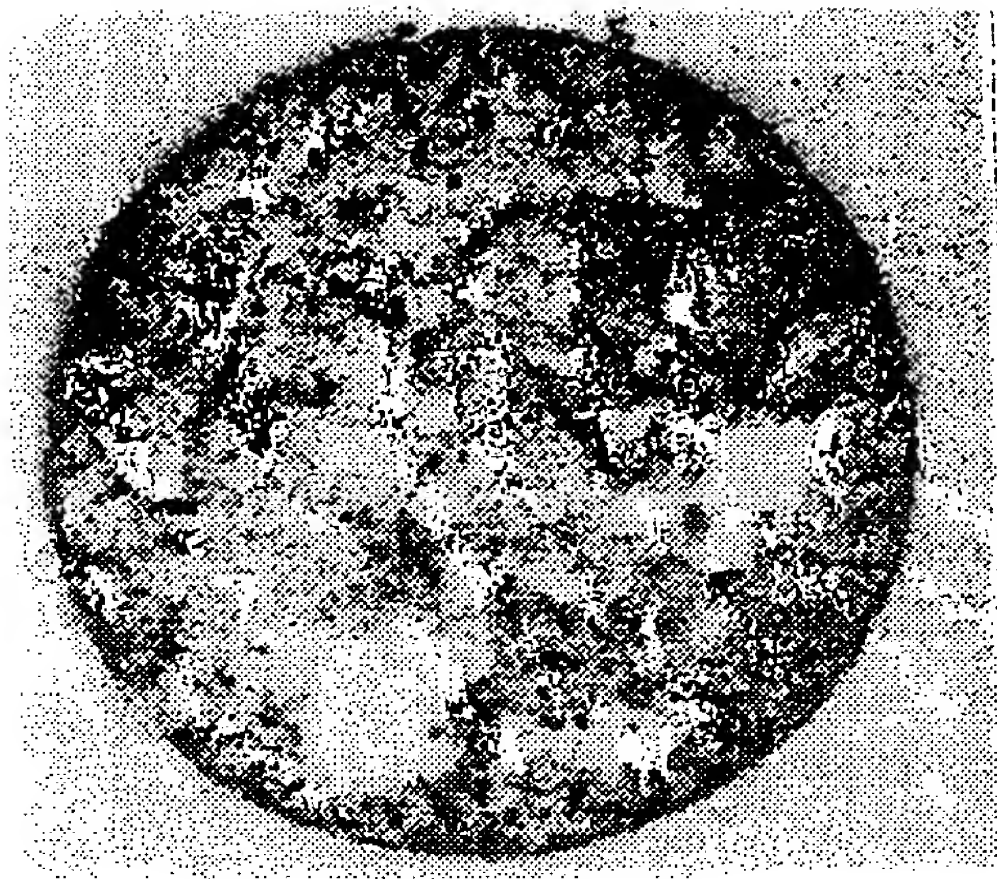


FIG. 6

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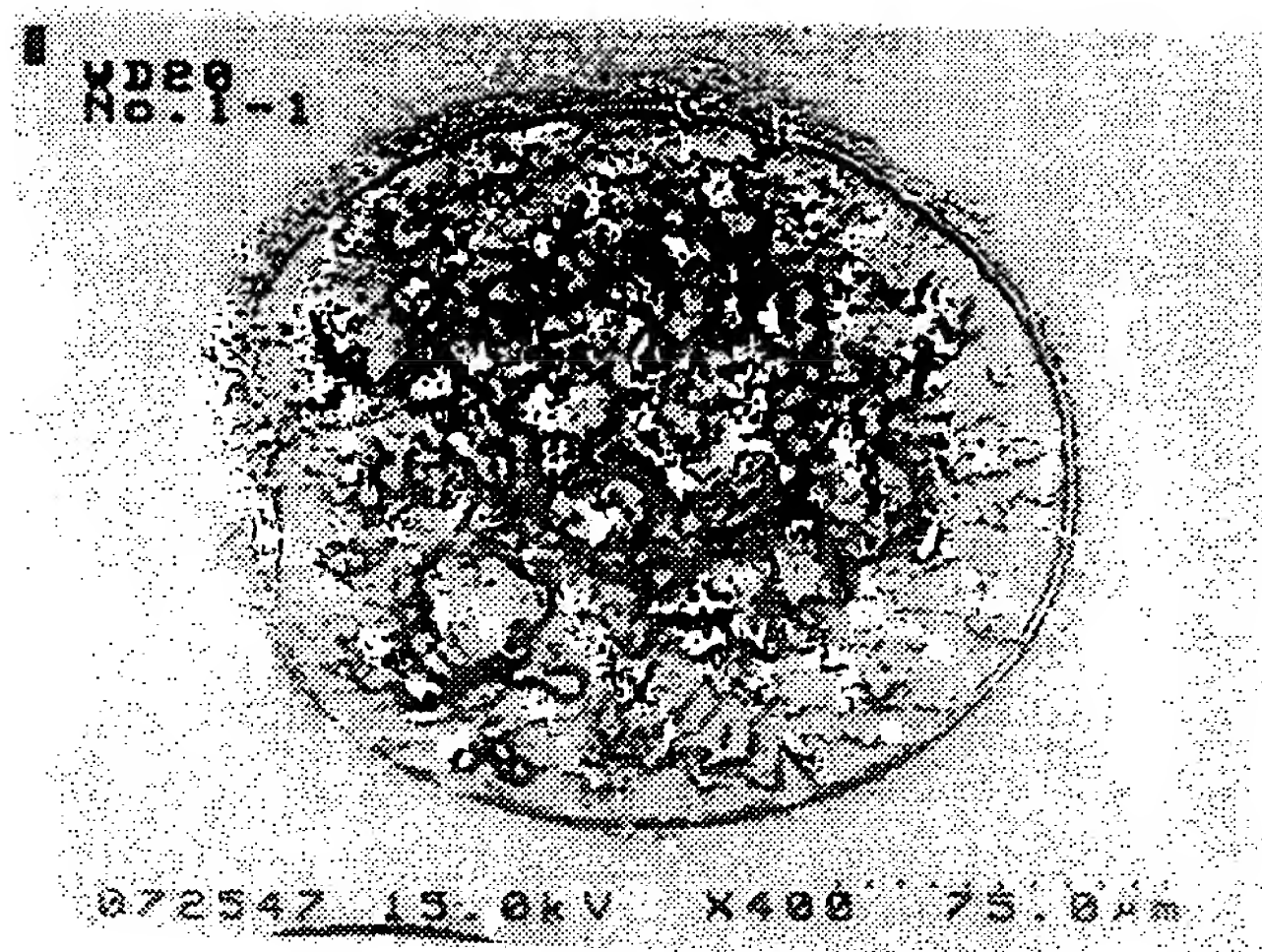


FIG. 7



FIG. 8

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FIG. 9

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FIG. 10

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FIG. 11

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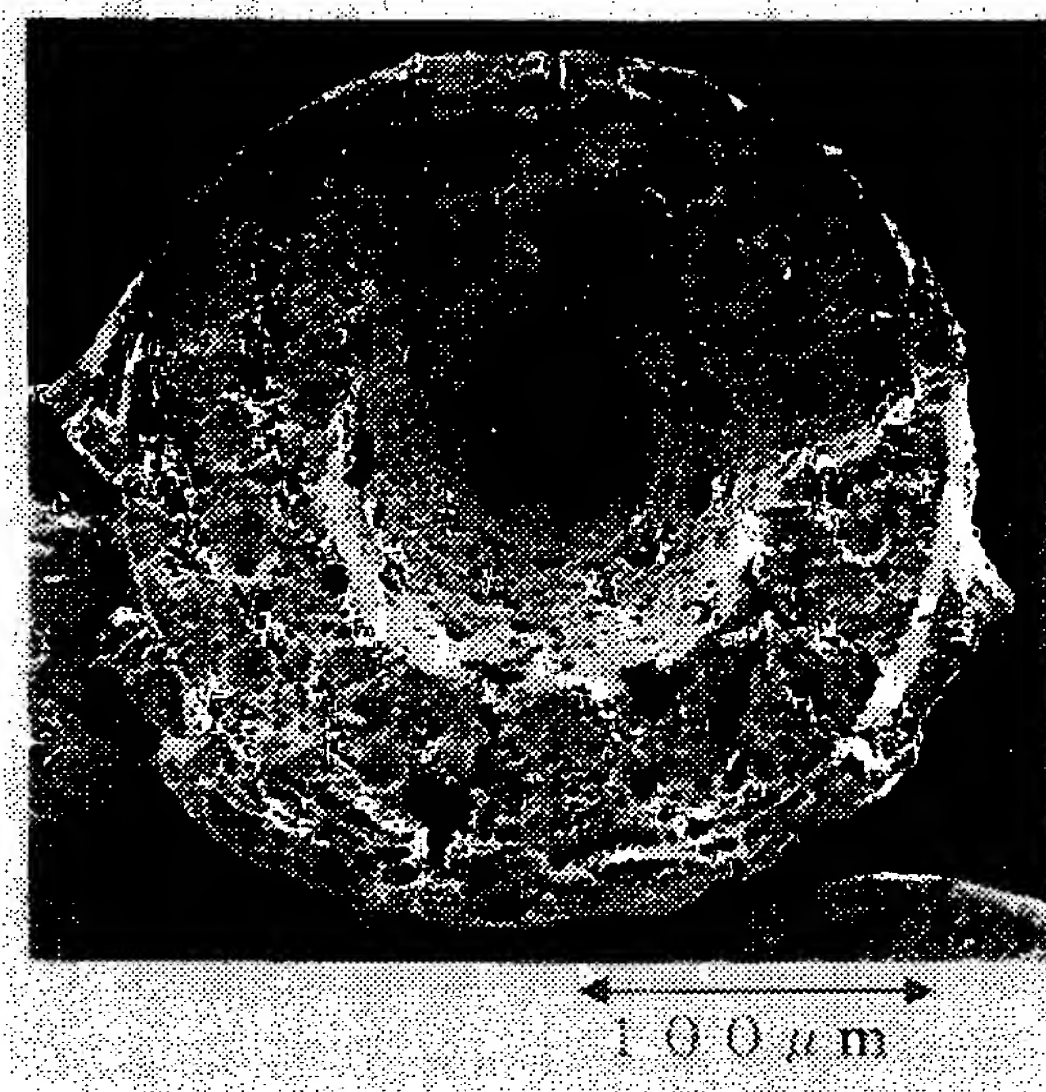


FIG. 12

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 98/05454

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/06 C11D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9708 Derwent Publications Ltd., London, GB; Class A97, AN 97-083705 XP002095864 & JP 08 325599 A (KAO CORP) , 10 December 1996 see abstract ---	1-3, 11
A	DE 44 39 418 A (UNILEVER NV) 18 May 1995 see claims ---	1-5
A	EP 0 229 671 A (KAO CORP) 22 July 1987 see page 26, line 13 - page 27, line 5; claims; example 4 ---	1-3
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

8 March 1999

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Int. .onal Application No
PCT/JP 98/05454

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	DATABASE WPI Section Ch, Week 9021 Derwent Publications Ltd., London, GB; Class D25, AN 90-160780 XP002095865 & JP 02 103297 A (LION CORP) , 16 April 1990 see abstract ---	1-3
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Information on patent family members

International Application No

PCT/JP 98/05454

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